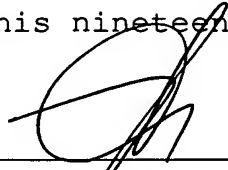


DECLARATION

I, Takashi Ota, the translator of the attached document,  
do hereby certify that to the best of my knowledge and belief,  
the attached document is true English translation of Japanese  
Patent Application No. 2002-358435.

Signed, this nineteenth day of July, 2007



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[Title of the Invention]   Image Forming Method and Apparatus  
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[Title of the Invention] Image Forming Method and Apparatus

[Scope of Claims]

[Claim 1]

5 An image forming method using a fixing method for heating  
and fixing a toner image on a recording medium with a heating  
element, one or more heating media heated by the heating element  
and a pressure member for causing the recording medium to be in  
press contact with one of the heating media, the image forming  
method being characterized in that at least one of the heating  
10 media is a belt-shaped heating medium used by being applied with  
a fixed amount of oil or no oil on a belt, and toner comprising  
at least a binder resin and a releasing agent as main components  
is used, wherein the toner has a weight average particle size of  
from 3.0 to 7.0  $\mu\text{m}$ , particle size distribution of  $1.00 \leq D_v/D_n \leq$   
15 1.25 (Dv: weight average particle size, Dn: number average  
particle size) and an average shape factor SF-1 of from 100 to  
150, and contains toner particles having SF-1 of 160 or more in  
an amount of 10 % by number or less.

[Claim 2]

20 The image forming method as described in claim 1,  
characterized in that a weight average particle size of toner is  
from 3.0 to 5.0  $\mu\text{m}$ .

[Claim 3]

25 The image forming method as described in claim 1 or 2,  
characterized in that particle size distribution of toner is  $1.00 \leq D_v/D_n \leq 1.20$  (Dv: weight average particle size, Dn: number  
average particle size).

[Claim 4]

30 The image forming method as described in any one of claims 1  
to 3, characterized in that an average shape factor SF-1 of toner  
is from 100 to 130.

[Claim 5]

The image forming method as described in any one of claims 1

to 4, characterized in that a ratio of toner particles having a shape factor SF-1 of 150 or more is 10 % by number or less.

[Claim 6]

5 The image forming method as described in any one of claims 1 to 5, characterized in that the toner has in a spindle shape.

[Claim 7]

The image forming method as described in any one of claims 1 to 6, characterized in that the toner has in the spindle shape, a ratio ( $r_2/r_1$ ) of a major axis  $r_1$  to a minor axis  $r_2$  is from 0.5 to 10 0.8, and a ratio ( $r_3/r_2$ ) of thickness  $r_3$  to the minor axis  $r_2$  is from 0.7 to 1.0.

[Claim 8]

The image forming method as described in any one of claims 1 to 7, characterized in that a releasing agent being one of toner 15 components has a melting point of from 60 to 120 °C, and is contained in an amount of from 1 to 20 % by weight.

[Claim 9]

The image forming method as described in any one of claims 1 to 8, characterized in that releasing agent particles having 20 dispersion diameter sizes of from 0.1 to 3  $\mu\text{m}$  in the toner occupy 80 % by number or more, and presence of the releasing agent is dispersed in the vicinity of particle surfaces by TEM observation.

[Claim 10]

25 The image forming method as described in any one of claims 1 to 9, characterized in that the toner has a storage modulus  $G'$  in a range of from  $5.5 \times 10^5$  to  $5.5 \times 10^7$  Pa at 80 °C and a storage modulus  $G'$  in a range of from  $5.0 \times 10^2$  to  $1.0 \times 10^4$  Pa at 180 °C, and shows a viscoelastic property in which a maximum 30 value of a ratio ( $\tan \delta = G''/G'$ ) of a loss modulus  $G''$  to the storage modulus is from 1.5 to 8.0 in a range of from 80 °C to 130 °C.

[Claim 11]

The image forming method as described in any one of claims 1 to 10, characterized in that an acid value of the binder resin being one of the toner components is from 1 to 50 mg KOH.

5 [Claim 12]

The image forming method as described in any one of claims 1 to 11, characterized in that the binder resin has a glass transition point of from 40 to 60 °C.

[Claim 13]

10 The image forming method as described in any one of claims 1 to 12, characterized in that the binder resin contains THF-insoluble contents in an amount of from 1 to 20 %.

[Claim 14]

15 The image forming method as described in any one of claims 1 to 13, characterized by using toner having a main peak in a region of a molecular weight of from 2,500 to 10,000 and a number average molecular weight in a range of from 2,500 to 50,000, in molecular weight distribution of tetrahydrofuran-soluble contents of a polyester resin contained in the toner.

20 [Claim 15]

The image forming method as described in any one of claims 1 to 14, characterized in that the toner is obtained by dissolving or dispersing, in an organic solvent, a prepolymer comprising a polyester resin having an isocyanate group, a compound capable of  
25 elongating or crosslinking with the prepolymer, and a toner component to cause the dissolved or dispersed matter to perform a crosslinking reaction and/or an elongation reaction in an aqueous medium, and removing the solvent from an obtained dispersion liquid.

30 [Claim 16]

An image forming apparatus comprising a fixing means for heating and fixing a toner image on a recording medium by using a heating element, one or more heating media heated by the heating

element, and a pressure member for causing the recording medium to be in press contact with one of the heating media, characterized in that at least one of the heating media is a belt-shaped heating medium used by being applied with a fixed amount of oil or no oil on a belt, and toner containing at least a binder resin and a releasing agent as main components is used, wherein the toner has a weight average particle size of from 3.0 to 7.0  $\mu\text{m}$ , particle size distribution of  $1.00 \leq D_v/D_n \leq 1.25$  (Dv: weight average particle size, Dn: number average particle size) and an average shape factor SF-1 of from 100 to 150, and contains toner particles having SF-1 of 160 or more in an amount of 10 % by number or less.

[Claim 17]

The image forming apparatus as described in claim 16, characterized in that the toner has a weight average particle size of from 3.0 to 5.0  $\mu\text{m}$ .

[Claim 18]

The image forming apparatus as described in claim 16 or 17, characterized in that the toner has particle size distribution of  $1.00 \leq D_v/D_n \leq 1.20$  (Dv: weight average particle size, Dn: number average particle size).

[Claim 19]

The image forming apparatus as described in any one of claims 16 to 18, characterized in that the toner has an average shape factor SF-1 of from 100 to 130.

[Claim 20]

The image forming apparatus as described in any one of claims 16 to 19, characterized in that toner particles having a shape factor SF-1 of 150 or more are contained in an amount of 10 % by number or less.

[Claim 21]

The image forming apparatus as described in any one of claims 16 to 20, characterized in that the toner has a spindle

shape.

[Claim 22]

The image forming apparatus as described in any one of claims 16 to 21, characterized in that the toner has the spindle shape, and a ratio ( $r_2/r_1$ ) of a major axis  $r_1$  to a minor axis  $r_2$  is from 0.5 to 0.8, and a ratio ( $r_3/r_2$ ) of thickness  $r_3$  to the minor axis  $r_2$  is from 0.7 to 1.0.

[Claim 23]

The image forming apparatus as described in any one of claims 16 to 22, characterized in that the releasing agent being one of the toner components has a melting point of from 60 to 120 °C, and is contained in an amount of from 1 to 20 % by weight.

[Claim 24]

The image forming apparatus as described in any one of claims 16 to 23, characterized in that releasing agent particles having dispersion diameter sizes of from 0.1 to 3  $\mu\text{m}$  occupy 80 % by number or more, and presence of the releasing agent is dispersed in the vicinity of particle surfaces by TEM observation.

[Claim 25]

The image forming apparatus as described in any one of claims 16 to 24, characterized in that the toner has a storage modulus  $G'$  in a range of from  $5.5 \times 10^5$  to  $5.5 \times 10^7$  Pa at 80 °C and a storage modulus  $G'$  in a range of from  $5.0 \times 10^2$  to  $1.0 \times 10^4$  Pa at 180 °C, and shows a viscoelastic property in which a maximum value of a ratio ( $\tan \delta = G''/G'$ ) of a loss modulus  $G''$  to the storage modulus is from 1.5 to 8.0 in a range of from 80 °C to 130 °C.

[Claim 26]

The image forming apparatus as described in any one of claims 16 to 25, characterized in that the binder resin being one

of the toner components has an acid value of from 1 to 50 mg KOH.  
[Claim 27]

The image forming apparatus as described in any one of  
claims 16 to 26, characterized in that the binder resin has a  
5 glass transition point of from 40 to 60 °C.  
[Claim 28]

The image forming apparatus as described in any one of  
claims 16 to 27, characterized in that the binder resin contains  
THF-insoluble contents in an amount of from 1 to 20 %.

10 [Claim 29]

The image forming apparatus as described in any one of  
claims 16 to 28, characterized by using toner having a main peak  
in a region of a molecular weight of from 2,500 to 10,000 and a  
number average molecular weight in a range of from 2,500 to  
15 50,000, in molecular weight distribution of  
tetrahydrofuran-soluble contents of a polyester resin contained  
in the toner.

[Claim 30]

The image forming apparatus as described in any one of  
20 claims 16 to 29, characterized in that the toner is obtained by  
dissolving or dispersing, in an organic solvent, a prepolymer  
comprising a polyester resin having an isocyanate group, a  
compound capable of elongating or crosslinking with the  
prepolymer, and a toner component to cause the dissolved or  
25 dispersed matter to perform a crosslinking reaction and/or an  
elongation reaction in an aqueous medium, and removing the  
solvent from an obtained dispersion liquid.

[Detailed Description of the Invention]

[0001]

30 [Technical Field]

The present invention relates to an image forming method and  
an image forming apparatus using toner for developing an  
electrostatic image for visualizing an electrostatic image formed



on a surface of a latent image carrier (photoconductor, or the like) in electrophotography, electrostatic recording, electrostatic printing, and the like.

[0002]

5 [Background Art]

Conventionally, in an image forming method using electrophotographic system, a latent image is formed by an electrostatic charge on an image carrier, such as a photoconductive substance, and forming a visible image by causing  
10 charged toner particles to adhere to the electrostatic latent image. The visible image formed by toner is finally transferred to a transfer medium, such as paper, and then fixed to the transfer medium by heat, pressure, a solvent gas, and the like to become an output image.

15 [0003]

The image forming method is roughly classified according to a method of charging toner particles for visualizing an image into a two-component development system using frictional electrification by stirring and mixing toner particles and  
20 carrier particles, and a one-component development system charging toner particles without using carrier particles. Further, the one-component development system is classified into a magnetic one-component development system and a nonmagnetic one-component development system according to whether or not  
25 magnetic force is used for holding toner particles on a development roller.

[0004]

On the other hand, in fixing in general, a method of melting toner with heat to fix the toner to an image carrier, such as  
30 paper, by directly press-contacting a fixing member, such as a fixing roller or a fixing belt, to an unfixed image is adopted in terms of thermal efficiency, simplicity of a fixing mechanism, production cost of the fixing member, and the like, that is, a

heat and pressure fixing method is adopted by preference.

In recent years in particular, a fixing mechanism using a belt-shaped heating medium (hereinafter referred to as belt fixing) is increasingly used for energy saving and reducing a size of an apparatus.

[0005]

According to the belt fixing, contact time of a belt to a toner surface may be extended during fixing, and fixing may be performed at a lower temperature. On the other hand, melting of the toner is accelerated to fusion bond the toner to a belt surface, that is, a toner offset phenomenon is easily caused. In color toner in particular, appropriate gloss is required for exhibiting sufficient transparency and high-definition feeling, and a molecular weight of a binder resin needs to be sharpened to obtain sharp melt characteristics. As a result, the melting of toner is promoted during fixing, and the toner offset phenomenon easily occurs.

As a fixing belt, an endless or regular belt made of a heat-resistant resin is used in many cases, and improvement in mechanical endurance is mentioned as a problem related to the fixing belt.

An external additive and the other components of the toner adhere to a belt-shaped heating medium which causes belt wear or damage, and hot offset and further a rupture of the fixing belt may occur.

[0006]

In order to solve the above-mentioned problems, various proposals are made on the fixing mechanism and toner for electrostatic image development.

For example, as a fixing mechanism, some investigations are made including a presentation "Discussion on On-demand Fixing Technique (A-11)" (Nonpatent document 1) in Japan Hardcopy '94 (June 23 - 24, 1994, sponsored by Society of Electrophotography

of Japan).

However, such investigations and proposals only for the fixing mechanism may not fundamentally solve the aforementioned problems for a same reason as described above.

5 [0007]

A fixing releasing material, such as wax, is known to be added to toner for preventing the offset in fixing. However, when wax characteristics or a dispersion state of the wax in the toner is inappropriate, phenomena, such as separation or bleeding of  
10 wax from a toner surface, occur due to long-term use within a development unit. In the two-component developer, occurrence of contamination or the like on a carrier surface deteriorates toner charge characteristics, and in the one-component developer, fused toner attaches to a development roller or a blade for thinning  
15 toner, and the like, thereby often inhibiting uniform toner development. Therefore, from a viewpoint of development, an amount of wax added is preferably low as much as possible.

[0008]

Toner conventionally obtained by a normal kneading and  
20 pulverizing method has generally an infinite form and problems of broad particle size distribution, low fluidity, low transfer property, high fixing energy, uneven electrostatic charge amount between toner particles, and low charge stability. In fixing in particular, since kneaded and pulverized toner prepared by a  
25 pulverization method breaks on a phase boundary of a releasing agent (wax) and mostly exists on a surface, release effect may be easily exhibited. On the other hand, the toner easily adheres to a carrier, a latent image carrier (photoconductor typically), and further to a blade, resulting in unsatisfactory performance.

30 [0009]

To overcome the problems of the toner according to the kneading and pulverizing method, a method of manufacturing toner according to a polymerization method is proposed. Since a

pulverization step is not included, the method does not require kneading and pulverization steps for toner manufacturing, and greatly contributes to cost reduction, such as energy saving, reduction of production time, and improvement in product yield.

5 In regard to particle size distribution in polymerized toner particles obtained by such a polymerization method, sharp distribution may be easily formed compared with particle size distribution of toner prepared by the pulverization method and  
10 capsulation of wax is also easy, and accordingly fluidity of toner may also be greatly improved. Further, spherical toner may be easily obtained.

However, toner by the polymerization method also has many problems not yet solved. Since surface tension acts in a polymerization process, the toner obtained by the polymerization  
15 method has particles with high sphericity as compared with the kneading and pulverizing method, but toner physical properties are not yet sufficient. Further the method does not easily control a toner shape (form a different shape). However, the method is advantageous to charge stability and a transfer  
20 property.

[0010]

In a toner manufacturing method by a suspension polymerization method widely used among polymerization methods, a monomer for a binder (binder resin) used for toner is limited to  
25 a styrene monomer or an acrylic monomer hazardous to a human body. Since the components are contained in the obtained toner, there is an environmental problem. Since the obtained toner capsulates wax, adhesion of the toner to a photoconductor is reduced when the toner is used in a real system. However, about  
30 the fixing property of the toner, since the wax is capsulated, the wax is hardly exposed to a toner surface compared with the pulverization method by which wax exists on a particle phase boundary, resulting in toner with bad fixing efficiency.

Therefore, the polymerized toner becomes toner disadvantageous in electric power consumption. Further, in a case of the polymerized toner, when an amount of wax is increased or a dispersion particle size of the wax is enlarged to improve fixability, transparency of a color image deteriorates when the polymerized toner is used as color toner. Therefore, the polymerized toner becomes unsuitable for toner for forming a presentation image by an overhead projector.

[0011]

There is an emulsion polymerization method in addition to the suspension polymerization method in the method of manufacturing polymerized toner. Also in the emulsion polymerization method, the monomer is limited to a styrene monomer. According to the method, unreacted monomers, an emulsifier, and a dispersing agent are difficultly removed completely from toner particles, and an environmental problem caused by the toner increasingly occurs.

[0012]

A dissolution-suspension method is known as a toner manufacturing method. The method has an advantage in that a polyester resin allowing low temperature fixation may be used. However, according to the method, a high molecular weight component is added in a step of dissolving or dispersing a low temperature fixing resin and a coloring agent to a solvent, which increases liquid viscosity, causing a problem of productivity. In the dissolution-suspension method, a surface shape of toner is formed spherical and the surface is formed in an irregular shape to improve cleaning characteristics of toner [Japanese Patent Laid-open Publication No. Hei9-15903 (Patent document 1)].

However, when wax is added to compositions of such toner as a releasing agent, uniform dispersibility and a dispersion state (surface presence) of wax and uniform dispersibility of a pigment deteriorate as compared with kneaded and pulverized toner, and a

degree of freedom for polymer design of a binder becomes complicated due to a restriction of viscosity since a high polymer becomes particles in a solvent, and therefore, releasability is difficultly secured.

5 [0013]

Japanese Patent Laid-open Publication No. Hei11-133665 (Patent document 2) proposes dry type toner having a practical sphericity of 0.90 to 1.00 and formed of an elongation reaction product of a urethane-modified polyester as a toner binder to  
10 improve toner fluidity, a low temperature fixing property, and hot offset resistance. Further, Japanese Patent Laid-open Publication No. Hei11-149180 (Patent document 3), Japanese Patent Laid-open Publication No. 2000-292981 (Patent document 4), and the like, disclose dry type toner having a small particle size  
15 excellent in powder fluidity and a transfer property; and excellent in all of heat-resistant storage stability, a low temperature fixing property and hot-offset resistance. Methods of manufacturing toner described in the publications include a step of increasing molecular weight in which an isocyanate  
20 group-containing polyester prepolymer is subjected to a polyaddition reaction with amine in an aqueous medium.

However, in the toner obtained by the above methods, distribution of a pigment or wax is inferior, and the pigment is unevenly dispersed in the toner, causing a problem of an image  
25 obtained by the toner showing low transparency, and inferior chroma saturation (brightness). Since there is no distribution control of a releasing agent being a releasing material in oilless fixation and oilless fixation toner is not designed in particular, mold release width may not be sufficiently provided.  
30 Further, when the toner is used for forming a color image on an OHP sheet, the image becomes dark due to a large dispersed particle size of the releasing agent.

[0014]

[Patent document 1] Japanese Patent Laid-open Publication  
No. Hei9-15903

[Patent document 2] Japanese Patent Laid-open Publication  
No. Hei11-133665

5 [Patent document 3] Japanese Patent Laid-open Publication  
No. Hei11-149180

[Patent document 4] Japanese Patent Laid-open Publication  
No. 2000-292981

10 [Nonpatent document 1] Presentation "Discussion on On-demand  
Fixing Technique (A-11)" in Japan Hardcopy '94 (June 23 - 24,  
1994, sponsored by Society of Electrophotography of Japan)

[0015]

[Problems to be Solved]

The present invention is made in view of the above problems,  
15 and an objective is to provide an image forming method and an  
apparatus capable of satisfying low temperature fixation,  
hot-offset resistance and heat-resistant storage stability for  
energy saving, gloss performance in color toner and transparency  
in overhead projector, and obtaining extremely stable and  
20 excellent image quality on actual use for a long periods, by  
clarifying interaction characteristics and an effective range of  
the characteristics between a belt-shaped heating medium used in  
a fixing part and toner for electrostatic charge development used  
in an image forming method using the fixing part.

25 [0016]

[Means for Solving Problems]

The present invention provides following matters (1) to  
(30).

(1) An image forming method using a fixing method for heating  
30 and fixing a toner image on a recording medium with a heating  
element, one or more heating media heated by the heating element  
and a pressure member for causing the recording medium to be in  
press contact with one of the heating media, the image forming

method being characterized in that at least one of the heating media is a belt-shaped heating medium used by being applied with a fixed amount of oil or no oil on a belt, and toner containing at least a binder resin and a releasing agent as main components is used, wherein the toner has a weight average particle size of from 3.0 to 7.0  $\mu\text{m}$ , particle size distribution of  $1.00 \leq D_v/D_n \leq 1.25$  ( $D_v$ : weight average particle size,  $D_n$ : number average particle size) and an average shape factor SF1 of from 100 to 150, and contains toner particles having SF-1 of 160 or more in an amount of 10 % by number or less.

[0017]

(2) The image forming method as described in (1), characterized in that a weight average particle size of toner is from 3.0 to 5.0  $\mu\text{m}$ .

[0018]

(3) The image forming method as described in (1) or (2), characterized in that particle size distribution of toner is  $1.00 \leq D_v/D_n \leq 1.20$  ( $D_v$ : weight average particle size,  $D_n$ : number average particle size).

[0019]

(4) The image forming method as described in any one of (1) to (3), characterized in that an average shape factor SF-1 of toner is from 100 to 130.

[0020]

(5) The image forming method as described in any one of (1) to (4), characterized in that a ratio of toner particles having a shape factor SF-1 of 150 or more is 10 % by number or less.

[0021]

(6) The image forming method as described in any one of (1) to (5), characterized in that the toner has a spindle shape.

[0022]

(7) The image forming method as described in any one of (1) to (6), characterized in that the toner has the spindle shape, a



ratio ( $r_2/r_1$ ) of a major axis  $r_1$  to a minor axis  $r_2$  is from 0.5 to 0.8, and a ratio ( $r_3/r_2$ ) of thickness  $r_3$  to the minor axis  $r_2$  is from 0.7 to 1.0.

[0023]

- 5        The image forming method as described in any one of (1) to (7), characterized in that a releasing agent being one of toner components has a melting point of from 60 to 120 °C, and is contained in an amount of from 1 to 20 % by weight.

[0024]

- 10       (9) The image forming method as described in any one of (1) to (8), characterized in that releasing agent particles having dispersion diameter sizes of from 0.1 to 3  $\mu\text{m}$  in the toner occupy 80 % by number or more, and presence of the releasing agent is dispersed in the vicinity of particle surfaces by TEM  
15 observation.

[0025]

- (10) The image forming method as described in any one of (1) to (9), characterized in that the toner has a storage modulus  $G'$  in a range of from  $5.5 \times 10^5$  to  $5.5 \times 10^7$  Pa at 80 °C and a storage  
20 modulus  $G'$  in a range of from  $5.0 \times 10^2$  to  $1.0 \times 10^4$  Pa at 180 °C, and shows a viscoelastic property in which a maximum value of a ratio ( $\tan \delta = G''/G'$ ) of a loss modulus  $G''$  to a storage modulus is from 1.5 to 8.0 in a range of from 80 °C to 130 °C.

- 25       [0026]

(11) The image forming method as described in any one of (1) to (10), characterized in that an acid value of the binder resin being one of the toner components is from 1 to 50 mg KOH.

[0027]

- 30       (12) The image forming method as described in any one of (1) to (11), characterized in that the binder resin has a glass transition point of from 40 to 60 °C.

[0028]

(13) The image forming method as described in any one of (1) to (12), characterized in that the binder resin contains THF-insoluble contents in an amount of from 1 to 20 %.

5 [0029]

(14) The image forming method as described in any one of (1) to (13), characterized by using toner having a main peak in a region of a molecular weight of from 2,500 to 10,000 and a number average molecular weight in a range of from 2,500 to 50,000, in  
10 molecular weight distribution of tetrahydrofuran-soluble contents of a polyester resin contained in the toner.

[0030]

(15) The image forming method as described in any one of (1) to (14), characterized in that the toner is obtained by dissolving  
15 or dispersing, in an organic solvent, a prepolymer formed of a polyester resin having an isocyanate group, a compound capable of elongating or crosslinking with the prepolymer and a toner component to cause the dissolved or dispersed matter to perform a crosslinking reaction and/or an elongation reaction in an aqueous  
20 medium, and removing the solvent from an obtained dispersion liquid.

[0031]

(16) An image forming apparatus including a fixing means for heating and fixing a toner image on a recording medium by using a  
25 heating element, one or more heating media heated by the heating element, and a pressure member for causing the recording medium to be in press contact with one of the heating media, characterized in that at least one of the heating media is a belt-shaped heating medium used by being applied with a fixed  
30 amount of oil or no oil on a belt, and toner containing at least a binder resin and a releasing agent as main components is used, wherein the toner has a weight average particle size of from 3.0 to 7.0  $\mu\text{m}$ , particle size distribution of  $1.00 \leq D_v/D_n \leq 1.25$

(Dv: weight average particle size, Dn: number average particle size) and an average shape factor SF-1 of from 100 to 150, and contains toner particles having SF-1 of 160 or more in an amount of 10 % by number or less.

5 [0032]

(17) The image forming apparatus as described in (16), characterized in that the toner has a weight average particle size of from 3.0 to 5.0  $\mu\text{m}$ .

[0033]

10 (18) The image forming apparatus as described in (16) or (17), characterized in that the toner has particle size distribution of  $1.00 \leq Dv/Dn \leq 1.20$  (Dv: weight average particle size, Dn: number average particle size).

[0034]

15 (19) The image forming apparatus as described in any one of (16) to (18), characterized in that the toner has an average shape factor SF-1 of from 100 to 130.

[0035]

20 (20) The image forming apparatus as described in any one of (16) to (19), characterized in that toner particles having a shape factor SF-1 of 150 or more are contained in an amount of 10 % by number or less.

[0036]

25 (21) The image forming apparatus as described in any one of (16) to (20), characterized in that the toner has a spindle shape.

[0037]

30 (22) The image forming apparatus as described in any one of (16) to (21), characterized in that the toner has the spindle shape, and a ratio ( $r_2/r_1$ ) of a major axis  $r_1$  to a minor axis  $r_2$  is from 0.5 to 0.8, and a ratio ( $r_3/r_2$ ) of thickness  $r_3$  to the minor axis  $r_2$  is from 0.7 to 1.0.

[0038]

(23) The image forming apparatus as described in any one of (16)

to (22), characterized in that the releasing agent being one of the toner components has a melting point of from 60 to 120 °C, and is contained in an amount of from 1 to 20 % by weight.

[0039]

- 5 (24) The image forming apparatus as described in any one of (16) to (23), characterized in that releasing agent particles having dispersion diameter sizes of from 0.1 to 3  $\mu\text{m}$  occupy 80 % by number or more, and presence of the releasing agent is dispersed in the vicinity of particle surfaces by TEM observation.

10 [0040]

- (25) The image forming apparatus as described in any one of (16) to (24), characterized in that the toner has a storage modulus  $G'$  in a range of from  $5.5 \times 10^5$  to  $5.5 \times 10^7$  Pa at 80 °C and a storage modulus  $G'$  in a range of from  $5.0 \times 10^2$  to  $1.0 \times 10^4$  Pa  
15 at 180 °C, and shows a viscoelastic property in which a maximum value of a ratio ( $\tan \delta = G''/G'$ ) of a loss modulus  $G''$  to the storage modulus is from 1.5 to 8.0 in a range of from 80 °C to 130 °C.

[0041]

- 20 (26) The image forming apparatus as described in any one of (16) to (25), characterized in that the binder resin being one of the toner components has an acid value of from 1 to 50 mg KOH.

[0042]

- (27) The image forming apparatus as described in any one of (16)  
25 to (26), characterized in that the binder resin has a glass transition point of from 40 to 60 °C.

[0043]

- (28) The image forming apparatus as described in any one of (16) to (27), characterized in that the binder resin contains  
30 THF-insoluble contents in an amount of from 1 to 20 %.

[0044]

- (29) The image forming apparatus as described in any one of (16)

to (28), characterized by using toner having a main peak in a region of a molecular weight of from 2,500 to 10,000 and a number average molecular weight in a range of from 2,500 to 50,000, in molecular weight distribution of tetrahydrofuran-soluble contents of a polyester resin contained in the toner.

[0045]

(30) The image forming apparatus as described in any one of (16) to (29), characterized in that the toner is obtained by dissolving or dispersing, in an organic solvent, a prepolymer formed of a polyester resin having an isocyanate group, a compound capable of elongating or crosslinking with the prepolymer and a toner component to cause the dissolved or dispersed matter to perform a crosslinking reaction and/or an elongation reaction in an aqueous medium, and removing the solvent from an obtained dispersion liquid.

[0046]

[Description of the Preferred Embodiments]

In the following, the present invention is described in more detail.

Fig. 1 shows an example of a fixing device used for an image forming method of the present invention. Here, a reference numeral 2 represents a fixing roller formed by coating a metallic core (aluminum, iron, or the like) with an elastic body (silicone rubber, or the like), and 1 represents a heating roller formed of a metallic core having a hollow cylinder shape (pipe formed of aluminum, iron, copper, stainless steel, or the like), and having a heat source 5 inside and the like. A reference numeral 7 represents a temperature sensor for measuring a surface temperature of a fixing belt 3 which contacts a portion of the heating roller 1. The fixing belt 3 is stretched between the fixing roller 2 and the heating roller 1. The fixing belt 3 has small heat capacity, and is formed by providing a releasing layer (having a thickness of from 50 to 300  $\mu\text{m}$  in a case of a silicone

rubber, approximately from 10 to 50  $\mu\text{m}$  in a case of a fluorocarbon resin, or the like) on a substrate (nickel, polyimide, or the like having a thickness of approximately from 30 to 150  $\mu\text{m}$ ). A reference numeral 4 represents a pressure roller formed by coating a metallic core with an elastic body, which forms a nip portion between the fixing belt 3 and the pressure roller 3 when the fixing roller 2 is pressed from below via the fixing belt 3.

Dimensions of each member are set according to various kinds of conditions required. In the drawing, 9 represents an oil application roller, 8 a guide, P a transfer medium, and T toner on the transfer medium.

The description represents only one example, and for example, a heat source may be provided in an inside of the fixing roller 2 or pressure roller 4, and the present invention may be applied to fixing devices using the fixing belt according to configurations other than the present example.

[0047]

The inventors of the present invention have examined wholeheartedly a fixing device using a belt fixing method, and a fixing property of toner, hot offset resistance, heat-resistant storage stability, and particularly glossiness of color toner and transparency in an overhead projector. As a result, the inventors find out that a particle size and a toner shape affect the characteristics, and particularly relate to the fixing property, and complete the present invention. Simultaneously, in dry type toner containing a modified polyester resin at least as a toner binder, the modified polyester exhibits effect as a dispersing agent having excellent pigment particles for forming a coloring agent, and satisfies toner fixing by the belt fixing method and the hot offset resistance while achieving distribution of the pigment particles and micro-dispersion of a releasing agent for increasing the transparency and glossiness of toner necessary for

color toner. The inventors of the present invention find out in particular a difference between the fixing device using a conventional belt fixing method and fixing according to a roller method, and come to complete the present invention.

5 [0048]

That is, a reason why a particle size and a shape of toner affect the fixing property of toner is likely because uniformity of a toner layer on paper has influence.

When an attention is paid to the particle size of toner, as  
10 a result of confirmation of the inventors, toner having a weight average particle size of from 3.0 to 7.0  $\mu\text{m}$  (preferably from 3.0 to 5.0  $\mu\text{m}$ ) and particle size distribution of  $1.00 \leq D_v/D_n \leq 1.25$  (preferably  $1.00 \leq D_v/D_n \leq 1.20$ ) ( $D_v$ : weight average particle size,  $D_n$ : number average particle size) exhibits an excellent  
15 fixing property. When an average particle size is less than 3.0  $\mu\text{m}$  or more than 7.0  $\mu\text{m}$ , and  $D_v/D_n$  larger than 1.25 even though the weight average particle size is from 3.0 to 7.0  $\mu\text{m}$ , inferior results are brought in the fixing property. The cause is assumed such that when a particle size and particle size distribution are  
20 in the above-mentioned ranges, the toner layer on the paper is uniformized, heat conduction is uniformly transmitted from the fixing member to the toner to uniformize a thermofusion state of toner, and the toner is fixed on the paper in the state. On the other hand, when a weight average particle size is less than 3.0  
25  $\mu\text{m}$  and surface unevenness of paper is particularly great, a fixing property may become insufficient because heat and pressure is not sufficiently transmitted from the fixing member to the toner entering recesses in the paper. When a weight average particle size exceeds 7.0  $\mu\text{m}$ , uniformity of the toner layer is  
30 insufficient and the fixing property may become insufficient because uniform heat is not transmitted.

[0049]

Toner exhibits an excellent fixing property by using toner having an averages shape factor SF-1 of from 100 to 150

(preferably from 100 to 130), and containing particles having SF-1 of 160 or more in an amount of 10 % by number or less

5 (preferably SF-1 of 150 or more in an amount of 10 % by number or less). In a case of the toner having the present shape factor, the toner layer on the paper is assumed to be further equalized, and heat is likely uniformly conducted from the fixing member to the toner to uniformize a thermofusion state of the toner.

10 [0050]

Toner preferably used in the present invention has a spindle shape.

An infinite form of toner in which a toner shape is not fixed, or a flat shape has inferior powder fluidity, causing  
15 following problems. Frictional electrification may not be smoothly performed, and a problem of a ground stain or the like easily occurs. Since dense and uniform toner arrangement is not formed when developing minute latent image dots, dot reproducibility is inferior. In an electrostatic transfer method,  
20 the toner is difficultly influenced by a line of electric force, and therefore, transfer efficiency is inferior.

When toner has a shape close to true sphericity, powder fluidity is excessive and the toner excessively acts upon external force, causing a problem of toner particles which easily  
25 scatter outside a dot at the time of development and transfer. Further, spherical toner easily rolls on a photoconductor, and entering between the photoconductor and a cleaning member, causing a problem of a cleaning defect in many cases.

[0051]

30 Powder fluidity of the spindle-shaped toner according to the present invention is adjusted moderately, and the frictional electrification is smoothly performed so as not generate ground stains, and the toner of the present invention is orderly



developed with respect to minute latent image dots, then efficiently transferred, and excels in dot reproducibility.

Further, the powder fluidity moderately applies brakes and scattering at the time is prevented. In a case of the

5 spindle-shaped toner, a rolling axis is limited as compared with spherical toner, and a cleaning defect of entering under a cleaning member hardly occurs.

[0052]

The spindle-shaped toner preferably has a ratio ( $r_2/r_1$ ) of a  
10 major axis to a minor axis of from 0.5 to 0.8, and a ratio ( $r_3/r_2$ ) of thickness to the minor axis from 0.7 to 1.0.

When a ratio ( $r_2/r_1$ ) of a major axis to a minor axis is less than 0.5, toner has a shape different from a true spherical shape, cleanability is high, but dot reproducibility and transfer  
15 efficiency are inferior, and high-definition image quality may not be obtained.

When a ratio ( $r_2/r_1$ ) of a major axis to a minor axis exceeds 0.8, a shape of toner approaches a spherical shape, and a cleaning defect may occur particularly under an environment of a  
20 low temperature and low humidity. When a ratio ( $r_3/r_2$ ) of thickness to a minor axis is less than 0.7, a shape of toner is close to a flat shape. In the case, although there are few scatterings as infinite form toner, a high transfer rate as the spherical toner is not obtained. When a ratio ( $r_3/r_2$ ) of the  
25 thickness to a minor axis is 1.0 in particular, a shape of toner has a rotating body using the major axis as a rotating axis. By forming a spindle shape close to the above rotating body, a shape which is not infinite, flat, or spherical is obtained, that is, a shape satisfying all of frictional electrification, dot  
30 reproducibility, transfer efficiency, prevention of scatterings, and cleanability is obtained.

[0053]

The binder resin in the toner used in the present invention

is particularly a polyester resin and or a polyester modified with a urea group or the like, and secures a low temperature fixing property and transparency of color toner. In order to obtain more sufficient releasability, micro-dispersion of wax is performed, and in order to promptly elute the releasing agent from the toner particles during fixing, dispersed particles of the releasing agent are caused to exist in the vicinity of particle surfaces, whereby sufficient releasability may be secured.

[0054]

Specifically, releasing agent particles inside the toner have dispersion diameter sizes of from 0.1 to 3  $\mu\text{m}$  and occupy 70 % by number or more. Presence of the releasing agent is dispersed in the vicinity of surfaces of the toner particles by TEM observation, resulting in high releasability in fixing. Many quality problems in pulverized toner caused by a releasing agent exposed on a surface, for example, spent to a carrier, filming to a photoconductor, developer quality deterioration due to a charge fluctuation, and the like, may be prevented

[0055]

Wax is dispersed by using usual mixing and an agitator. Specifically, a raw material solution in which the releasing agent is dissolved is stirred with a dissolution stirring tank or the like, and wet milling is performed by using a device equipped with granular media, such as an attritor, ball mill, sand mill, vibration mill, or the like. As granular media, steel, such as stainless steel and carbon steel, alumina, zirconia, silica, or the like, is preferably used.

[0056]

In a method of dissolving or dispersing a toner composition in an organic solvent to obtain toner particles in an aqueous medium, polar group portions in the modified polyester exhibit compatibility with water, and are selectively concentrated on

toner surfaces, which produce an effect of preventing the releasing agent particles from being exposed to the surfaces.

That is, the toner of the present invention is capsulated in a state where the releasing agent is micro-dispersed in the

5 particles. There is not a bad influence such as filming or charge stability inhibition caused by a large wax dispersion diameter size or existence in the vicinity of the surface.

[0057]

10 That is, the toner of the present invention is capsulated in a state where the releasing agent is micro-dispersed in the particles, and there is not a bad influence such as filming or charge stability inhibition caused by a large wax dispersion diameter size or existence in the vicinity of the surface.

[0058]

15 Further, in the present invention, a pigment may be fed simultaneously with the releasing agent and dispersed. Coagulation of the coloring agent is solved with the agitator, thereby dispersing an average particle size of the coloring agent until the size becomes 0.7  $\mu\text{m}$  or less, and preferably 0.4  $\mu\text{m}$  or  
20 less. Therefore, the toner excels also in glossiness and transparency as color toner, and a clear image excellent in color reproduction may be obtained.

[0059]

25 In the present invention, a particle size in a largest direction of the releasing agent is defined as a dispersion diameter size of the releasing agent. Specifically, toner is embedded in an epoxy resin, and sliced in ultrathin section of approximately 100 nm, and dyed with ruthenium tetroxide. The ultrathin sections are observed with a transmission electron  
30 microscope (TEM) at a magnification of 10,000 times, and a photograph is taken and visually evaluated to observe a dispersion state of the releasing agent to determine a dispersion diameter size.

[0060]

The dispersion diameter sizes of the releasing agent existing in the toner of the present invention and having particle sizes of from 0.1 to 3  $\mu\text{m}$  are 80 % by number or more, more preferably the dispersion diameter sizes of the releasing agent having particle sizes of from 1 to 2  $\mu\text{m}$  are 70 % by number or more. When there are many small particles less than 0.1  $\mu\text{m}$ , sufficient releasability may not be exhibited. When there are many particles exceeding 3  $\mu\text{m}$ , a cohesive property is exhibited, and fluidity deteriorates or filming occurs. Thus, color reproducibility and glossiness are markedly reduced in color toner.

[0061]

The releasing agent used in the present invention may be selected from publicly known releasing agents, and examples include polyolefin wax (polyethylene wax, polypropylene wax, or the like); long chain hydrocarbon (paraffin wax, Sasol wax, or the like); carbonyl group-containing wax, or the like. Among the examples, carbonyl group-containing wax is preferable. Examples of the carbonyl group-containing wax include poly alkane acid ester (carnauba wax), montan wax, trimethylolpropane tribehenate, pentaerythritol tetrabehenate, pentaerythritol diacetate dibehenate, glycerine tribehenate, 1,18-octadecanediol distearate or the like; polyalkanol ester (tristearyltrimellitic acid, distearyl maleate or the like); poly alkane acid amide (ethylenediamine dibehenyl amide or the like); polyalkylamide (trimellitic acid tristearylamide or the like); and dialkyl ketones (distearyl ketone or the like), and the like. Among the carbonyl group-containing wax, poly alkane acid ester is preferable.

[0062]

Dry type toner according to the present invention has a storage modulus  $G'$  in a range of from  $5.5 \times 10^5$  to  $5.5 \times 10^7$  Pa at

80 °C and a storage modulus  $G'$  in a range of from  $5.0 \times 10^2$  to  $1.0 \times 10^4$  Pa at 180 °C, and a maximum value of a ratio ( $\tan \delta = G''/G'$ ) of a loss modulus  $G''$  to the storage modulus is from 1.5 to 8.0 in a range of 80 °C to 130 °C. The dry type toner having the above  
5 viscoelastic properties is capable of securing sufficient releasability in the belt method while maintaining transparency in OHP which may not be achieved by the conventional belt fixing. The inventors of the present invention consider the reasons therefor as follows.

10 [0063]

That is, fixing to paper in the roller fixing or the belt fixing is estimated to start in the vicinity of 80 °C to 120 °C when a fixing effective temperature of toner is observed with a thermolabel or the like. As a result of investigation of the  
15 present toner on a relationship between a melting temperature and melt viscosity in belt fixing of toner based on the fixing effective temperature of toner, when a relationship between toner fixing and the viscoelasticity is expressed with viscoelasticity, if a storage modulus  $G'$  of the toner is not  $5.5 \times 10^7$  Pa or less  
20 at 80 °C, an elastic modulus is high and fixing hardly occurs. Fixing occurs smoothly in the viscoelasticity range because the polyester resin being the binder has good affinity with the paper. The belt fixing is performed at a lower fixing pressure unlike the roller fixing, and a heat characteristic design and  
25 particle structure control of the binder are required to satisfy fixing, hot offset resistance, and glossiness of color toner, and the toner constituent particles of the present invention exhibits performance.

[0064]

30 Conditions for a belt fixing unit are:

belt tension: 1.5 kg/piece,

belt speed: 170 mm/sec,

fixation nip width: 10 mm,

fixing roller: (roller diameter:  $\Phi 38$  mm),  
surface material and hardness: a silicon foam having  
approximately 30 degrees (Asker (R) C hardness),  
pressure roller: (roller diameter:  $\Phi 50$  mm),  
5 surface material and hardness: PFA tube + silicone rubber  
having a thickness of 1 mm, and approximately 75 degrees (Asker  
(R) C hardness),  
diameter of metallic core:  $\Phi 48$  mm (iron, wall thickness 1  
mm),

10 heating roller: (roller diameter:  $\Phi 30$  mm, (aluminum, wall  
thickness 2 mm)), and

fixing belt: (belt diameter:  $\Phi 60$  mm, substrate: Nickel  
having a thickness of approximately 40  $\mu$ m, releasing layer:  
silicone rubber having approximately 150  $\mu$ m, belt width 310 mm).

15 A case of  $5.5 \times 10^5$  Pa or less at 80 °C does not cause a problem  
of the fixing property, but does not satisfy the storage  
stability.

On the other hand, when a storage modulus  $G'$  is  $5.0 \times 10^2$  or  
less at 180 °C, elasticity of the binder necessary for the hot  
20 offset is not obtained. In a case of  $1.0 \times 10^4$  Pa or more, the  
hot offset resistance is sufficiently satisfied, but elasticity  
is too high and temperature of a low temperature fixing property  
is increased. In belt fixing at low fixing pressure, sufficient  
gloss is not obtained, if viscosity of the binder is not  
25 sufficiently high after toner start fixing to satisfy glossiness  
of color toner.

[0065]

Sufficient viscosity is required in the fixing at from 80 to  
130 °C at which the fixing starts, and is indicated by a  
30 viscoelastic property  $\tan \delta$  (a ration of a loss modulus  $G''$  to the  
storage modulus:  $\tan \delta = G''/G'$ ). The values for satisfying the

glossiness are from 1.5 to 8.0 according to experimental results. In a case less than 1.5, the glossiness is not obtained. In a case exceeding 8.0, the glossiness is satisfied, but the hot offset is not satisfied.

5 [0066]

The toner of the present invention is effective to the hot offset and the glossiness probably because the pigment dispersibility and dispersibility of the releasing agent are exhibited even if melting begins at a relatively low temperature at 80 °C, G' does not decrease from 150 °C to 180 °C, and cohesive force of the toner binder does not decrease in belt fixing to maintain releasability.

[0067]

15 As a method of measuring viscoelasticity, RheoStress RS 50 made by HAAKE is used by immobilizing 1 g of a sample on a parallel plate of 20 mm at a frequency of 1 Hz, temperature of from 70 to 210 °C, and a heating rate of 3 °C/min.

[0068]

20 A melting point of the releasing agent used is from 60 to 120 °C, and when the releasing agent is contained in an amount of from 1 to 20 wt%, a necessary amount of releasing agent exudes from the toner surface in fixing, and sufficient offset resistance is obtained.

[0069]

25 An acid number of the binder resin used for the toner is preferably from 1 to 50 mg KOH (particularly preferably from 5 to 30 mg KOH). Tg is from 40 to 65 °C, preferably from 45 to 60 °C. A number average molecular weight Mn is from 2,500 to 50,000, preferably from 2,500 to 30,000. A weight average molecular weight Mw is from 5,000 to 100,000, preferably from 10,000 to 50,000.

[0070]

The toner of the present invention is obtained by dissolving

or dispersing, in an organic solvent, a prepolymer formed of a polyester resin having an isocyanate group, a compound capable of elongating or crosslinking with the prepolymer and a toner component to cause the dissolved or dispersed matter to perform a crosslinking reaction and/or an elongation reaction in an aqueous medium, and removing the solvent from an obtained dispersion liquid. As a result, the particle size and the shape of the present invention may be achieved, and the fixing property may be improved, and further the offset resistance in fixing may be improved.

In the method of dissolving or dispersing, in the organic solvent, the toner composition, and dispersing the toner composition in the aqueous medium to obtain the toner particles in particular, polar group portions in the modified polyester exhibit affinity with water and selectively concentrate in the toner surface, thereby also producing an effect of preventing the particles of the releasing agent from being exposed from the surface.

That is, toner of the present invention is capsulated in a state where wax is micro-dispersed in the particles, and there is no influence, such as filming and charge stability inhibition, due to a large dispersion diameter size of the releasing agent or existence in the vicinity of the surface.

[0071]

The toner of the present invention generally contains a coloring agent, and to obtain the toner in which the coloring agent is uniformly dispersed, a manufacturing condition of toner is required to be devised, and the above-mentioned toner having high quality may not be obtained according to a conventional manufacturing condition.

In the present invention, to obtain the quality toner, when forming an oily dispersion liquid containing the prepolymer, the coloring agent, and the releasing agent, a step (wet milling



step) of pulverizing the coloring agent is necessary. As a wet milling device for performing the wet milling step in the case, any devices may be used as long as the devices are capable of pulverizing the coloring agent in the liquid by providing impact force to the coloring agent. Examples of such devices include conventionally known various types of wet milling devices, such as a ball mill and bead mill.

In the wet milling step, the temperature is from 5 to 20 °C, preferably from 15 to 20 °C.

By adjusting the wet milling conditions, a dispersed particle size and particle size distribution of the coloring agent contained in the toner particles may be controlled in the above-mentioned range. The wet milling step is applicable also to the dispersion liquid after reaction when necessary.

[0072]

The average particle size and the particle size distribution of toner are measured by a Coulter Counter method. Examples of measuring devices of the particle size distribution of the toner particles include Coulter Counter TA-II and Coulter Multisizer II (all are made by Beckman Coulter, Inc.). In the present invention, measurement is performed by using Coulter Counter TA-II type connected with an Inter Face (made by Institute of Japanese Union of Science & Engineers) which outputs number distribution and volume distribution, and the PC 9801 personal computer (made by NEC).

[0073]

(Method of measuring weight average particle size and number average particle diameter of toner)

First, 0.1 to 5 ml of a surfactant (preferably alkylbenzene sulfonate) is added as a dispersing agent to 100 to 150 ml of an electrolyte. Here, the electrolyte is an approximately 1 % NaCl solution prepared by using first grade sodium chloride. For example, ISOTON-II (made by Beckman Coulter, Inc.) may be used.

Here, 2 to 20 mg of measurement samples is further added. The electrolyte in which the test samples are suspended is dispersed for approximately 1 to 3 minutes by using an ultrasonic dispersion device, and volume distribution and number distribution are calculated by measuring a volume and a number of toner particles by using the measuring device and a 100  $\mu\text{m}$  aperture as an aperture.

As channels, a total of 13 channels of less than 2.00 to 2.52  $\mu\text{m}$ ; less than 2.52 to 3.17  $\mu\text{m}$ ; less than 3.17-4.00  $\mu\text{m}$ ; less than 4.00-5.04  $\mu\text{m}$ ; less than 5.04 to 6.35  $\mu\text{m}$ ; less than 6.35 to 8.00  $\mu\text{m}$ ; less than 8.00 to 10.08  $\mu\text{m}$ ; less than 10.08 to 12.70  $\mu\text{m}$ ; less than 12.70 to 16.00  $\mu\text{m}$ ; less than 16.00 to 20.20  $\mu\text{m}$ ; less than 20.20 to 25.40  $\mu\text{m}$ ; less than 25.40 to 32.00  $\mu\text{m}$ ; and 32.00 to 40.30  $\mu\text{m}$  is used. Objects are particles having particle sizes of from 2.00  $\mu\text{m}$  or more to less than 40.30  $\mu\text{m}$ . The weight average particle size ( $D_v$ ) of a volume reference determined by the volume distribution related to the toner of the present invention, and the number average particle diameter ( $D_n$ ) determined by the number distribution are determined, and the ratio  $D_v/D_n$  is calculated.

[0074]

(Method of measuring shape factor SF-1)

In the present invention, 100 toner images at a magnification of 500 times are randomly sampled by using, for example Hitachi FE-SEM (S-800) with SF-1, and image information is introduced in an image analyzing device made by NIRECO Corporation (Luzex III) via an interface, and then a value obtained by a calculation according to a following equation is defined as the shape factor SF-1.

$$\text{SF-1} = \{ (M \times \text{LNG})^2 / \text{AREA} \} \times (100 \pi / 4)$$

[In the equation,  $M \times \text{LNG}$  indicates an absolute maximum length of the toner particle and AREA indicates a projected area

of the toner particle.]

The shape factor SF-1 indicates a degree of roundness of the toner particle.

The toner particle produced by the melt kneading and pulverization method has an infinite form, and a shape factor SF-1 of the toner particle generally exceeds 150.

[0075]

(A method of measuring spindle-shaped major axis  $r_1$ , minor axis  $r_2$ , and thickness  $r$ )

As shown in Fig. 2,  $r_1$ ,  $r_2$  and  $r_3$  are measured by using a scanning electron microscope (SEM) while changing an angle of a visual field, taking a photograph and observing the photograph.

[0076]

(Method of measuring molecular weight distribution of binder resin component)

The molecular weight distribution of the binder resin component contained in the toner according to the present invention is measured as follows by using GPC.

A column is stabilized in a heat chamber at 40 °C, and THF is passed at a flow rate of 1 ml/min as a column solvent at the temperature. A THF sample solution of a resin adjusted to 0.05 to 0.6 % by weight as sample concentration is injected in an amount of 50 to 200  $\mu$ l, and a measurement operation is performed.

In the determination of molecular weight of the test sample, molecular weight distribution which the test sample has are calculated from a relationship between a logarithm of a calibration curve prepared by several kinds of monodisperse polystyrene standard samples and the count numbers. As the standard polystyrene test samples for preparing the calibration curve, at least approximately 10 standard polystyrene test samples are used, including samples each having a molecular weight of  $6 \times 10^2$ ,  $2.1 \times 10^2$ ,  $4 \times 10^2$ ,  $1.75 \times 10^4$ ,  $1.1 \times 10^5$ ,  $3.9 \times 10^5$ ,  $8.6 \times 10^5$ ,  $2 \times 10^6$ , and  $4.48 \times 10^6$  made by Pressure

Chemical Co. or Tosoh Corporation. Further, an RI (refractive index) detector is used for a detector.

[0077]

Examples of the method of manufacturing the toner of the present invention include (1) a method of pulverizing and classifying constituent materials of toner after melt kneading, (2) a method of suspending and polymerizing a radically polymerizable monomer composition containing a coloring agent and a chain transfer agent in an aqueous medium, (3) a method of subjecting to emulsion polymerization a radically polymerizable monomer composition containing a chain transfer agent in an aqueous medium by using a water soluble polymerization initiator, and fusion-bonding obtained resin particles in an aqueous medium, and the like, but (4) a method of obtaining toner by dissolving or dispersing, in an organic solvent, a prepolymer containing a polyester resin having an isocyanate group, a compound capable of elongating or crosslinking with the prepolymer and a toner component to cause the dissolved or dispersed matter to perform a crosslinking reaction and/or an elongation reaction in an aqueous medium, and removing the solvent from an obtained dispersion liquid is particularly preferable to achieve the objective of the present invention.

[0078]

In the case, the polyester prepolymer containing the isocyanate group may be obtained by preparing polyester having an active hydrogen group by polycondensation between polyol (PO) and polycarboxylic acid (PC), and further causing the polyester to react with polyisocyanate (PIC).

In the case, the active hydrogen group which the polyester has includes, for example, hydroxyl groups (alcoholic hydroxyl group and phenolic hydroxyl group), amino groups, carboxyl groups, sulfhydryl groups, and the like, and the alcoholic hydroxyl group is preferable among the groups.

[0079]

Examples of the polyol (PO) include diol (DIO) and trivalent or higher polyol (TO), and (DIO) alone or a mixture of (DIO) and a small amount of (TO) is preferred.

5 [0080]

Examples of the diol (DIO) include alkylene glycol (ethylene glycol) 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butanediol, 1,6-hexandiol, and the like; alkylene ether glycol (diethylene glycol, triethylene glycol, dipropylene glycol, polyethylene glycol, polypropylene glycol, polytetramethylene ether glycol, and the like); alicyclic diol (1,4-cyclohexane dimethanol, Hydrogenation bisphenol A, and the like); bisphenols (bisphenol A, bisphenol F, bisphenol S, and the like); alkylene oxide (ethyleneoxide, propylene oxide, butylene oxide, and the like) adducts of the above alicyclic diol; alkylene oxide (ethyleneoxide, propylene oxide, butylene oxide, and the like) adducts of the above bisphenols, and the like. Among diols, the alkylene glycol having 2 to 12 carbon atoms, and alkylene oxide adducts of the bisphenols are preferable, and  
10  
15  
20  
alkylene oxide adducts of the bisphenols alone or in combination with the alkylene glycol having 2 to 12 carbon atoms are particularly preferable.

[0081]

Examples of the trivalent or higher polyol (TO) include  
25  
trivalent to octavalent or higher multivalent fatty alcohol (glycerine), trimethylolethane, trimethylolpropane, pentaerythritol, sorbitol, and the like); trivalent or higher phenol (trisphenol PA, phenol novolak, cresol novolak, and the like); alkylene oxide adducts of trivalent or higher polyphenol,  
30  
and the like.

[0082]

As the polycarboxylic acid (PC), dicarboxylic acid (DIC) and trivalent or higher polycarboxylic acid (TC) are mentioned, and a

mixture of DIC alone or in combination with a small amount of TC is preferred.

[0083]

Examples of the dicarboxylic acid (DIC) include alkylene  
5 dicarboxylic acid (succinic acid, adipic acid, sebacic acid, and the like); alkenylenedicarboxylic acid (maleic acid, fumaric acid, and the like); aromatic dicarboxylic acid (phthalic acid, isophthalic acid, terephthalic acid, naphthalene dicarboxylic acid, and the like), and the like. Among the dicarboxylic acids,  
10 alkenylenedicarboxylic acid having 4 to 20 carbon atoms, and aromatic dicarboxylic acid having 8 to 20 carbon atoms are preferred.

[0084]

Examples of the trivalent or higher polycarboxylic acid (TC)  
15 include aromatic polycarboxylic acid (trimellitic acid, pyromellitic acid, and the like) having 9 to 20 carbon atoms. In addition, the above-mentioned acid anhydride or the lower alkyl ester (methyl ester, ethyl ester, isopropyl ester, and the like) may be used as the polycarboxylic acid to cause to react the  
20 polycarboxylic acid with polyol.

[0085]

A ratio of polyol to polycarboxylic acid as an equivalent ratio  $[OH]/[COOH]$  of a hydroxyl group  $[OH]$  and a carboxyl group  $[COOH]$  is generally from 2/1 to 1/1, preferably from 1.5/1 to  
25 1/1, and more preferably from 1.3/1 to 1.02/1.

[0086]

Examples of the polyisocyanate (PIC) include aliphatic polyisocyanate (tetramethylene di-isocyanate, hexamethylene diisocyanate, 2,6-diisocyanatomethyl caproate, and the like);  
30 alicyclic polyisocyanate (isophorone diisocyanate, cyclohexylmethane diisocyanate, and the like); aromatic diisocyanate (tolylene diisocyanate, diphenylmethane diisocyanate, and the like); aromatic-aliphatic diisocyanate ( $\alpha, \alpha, \alpha', \alpha'$ -tetramethyl

xylylene diisocyanate, and the like); isocyanurates; blocked products of the polyisocyanate with a phenol derivative, oxime, caprolactam, or the like; and mixtures of two or more kinds of above-mentioned compounds.

5 [0087]

To obtain a polyester prepolymer having an isocyanate group, a ratio of a polyisocyanate (PIC) to a polyester resin (PE) having an active hydrogen group is generally 5/1 to 1/1, preferably 4/1 to 1.2/1, more preferably 2.5/1 to 1.5/1 as an  
10 equivalent ratio  $[NCO]/[OH]$  of the isocyanate group  $[NCO]$  and the hydroxyl group  $[OH]$  of the polyester having the hydroxyl group. When a ratio  $[NCO]/[OH]$  exceeds 5, the low temperature fixing property deteriorates. When a molar ratio of  $[NCO]$  is less than 1, a urea content in the ester decreases in a case of using  
15 modified polyester, and hot-offset resistance deteriorates.

[0088]

A content of the polyisocyanate (PIC) component in the prepolymer (A) having the isocyanate group at the end is generally from 0.5 to 40 % by weight, preferably from 2 to 20 %  
20 by weight, more preferably from 1 to 30 % by weight. When a content is less than 0.5 % by weight, the hot-offset resistance deteriorates, both of the heat-resistant storage stability and the low temperature fixing property may not be satisfactorily satisfied. When a content exceeds 40 % by weight, the low  
25 temperature fixing property deteriorates.

[0089]

The isocyanate group contained in one molecule in the polyester prepolymer (A) having the isocyanate group, is generally 1 or more, preferably from 1.5 to 3 in average, and  
30 more preferably from 1.8 to 2.5 in average. When an isocyanate group is less than 1 per molecule, a molecular weight of urea modified polyester obtained becomes low, and the hot-offset resistance deteriorates.

[0090]

A urea-modified polyester resin (UMPE) may be obtained from the polyester prepolymer (A) having the isocyanate group by causing the polyester prepolymer (A) to react with an amine (B).

5 The urea-modified polyester resin exhibits an excellent effect as a toner binder.

[0091]

Examples of the amines (B) include diamine (B1), trivalent or higher polyamine (B2), amino alcohol (B3), aminomercaptan  
10 (B4), amino acid (B5), and amino-blocked products (B6) of the amines B1 to B5.

[0092]

Examples of the diamine (B1) include aromatic diamine (phenylenediamine, diethyltoluenediamine,  
15 4,4'-diaminodiphenylmethane and the like); alicyclic diamine (4,4'-diamino-3,3'-dimethyl dicyclohexyl methane, diamine cyclohexane, isophoronediamine, and the like); and aliphatic diamine (ethylenediamine, tetramethylenediamine, hexamethylenediamine, and the like) and the like.

20 Diethylenetriamine, triethylenetetramine, and the like are mentioned as the trivalent or higher polyamine (B2).

Ethanolamine, the hydroxyethylaniline, and the like are mentioned as the amino alcohol (B3).

25 Aminoethyl mercaptan, aminopropyl mercaptan, and the like are mentioned as the aminomercaptan (B4).

Aminopropionic acid, aminocaproic acid, and the like are mentioned as the amino acid (B5).

30 Examples of the amino-blocked products (B6) of the amines B1 to B5 include a ketimine compound, an oxazolidine compound, and the like which are obtained from the amines B1 to B5 and ketone (acetone, methyl ethyl ketone, methyl isobutyl ketone, and the like) and the like.

Among the amines (B), B1 alone or in combination with a



small amount of B2.

[0093]

When causing the prepolymer A to react with the amine B, a molecular weight of the polyester may be adjusted by using an elongation terminator when necessary. Examples of the elongation terminator include monoamine (diethylamine, dibutyl amine, butylamine, lauryl amine, and the like) having no active hydrogen-containing group, blocked products thereof (ketimine compound) and the like. The additive amount is suitably selected according to a desired molecular weight of a urea-modified polyester to be produced.

[0094]

A ratio of the amine (B) to the prepolymer (A) having the isocyanate group is generally from 1/2 to 2/1, preferably from 1.5/1 to 1/1.5, more preferably from 1.2/1 to 1/1.2 as equivalent ratio  $[NCO]/[NHx]$  of the isocyanate group  $[NCO]$  in the prepolymer (A) having the isocyanate group, and the amino group  $[NHx]$  ( $x$  indicates numbers of 1 to 2) in the amine (B). When a ratio of  $[NCO]/[NHx]$  exceeds 2, or is less than 1/2, a molecular weight of the polyester becomes low, and the hot-offset resistance deteriorates.

[0095]

In the present invention, when causing the isocyanate group-containing prepolymer A to react with the amine B in the aqueous medium, a polyester resin D being unreactive with the amine may be incorporated in the aqueous medium when necessary. The polyester resin D has a Tg of from 35 to 65 °C, preferably from 45 to 60 °C, and the Mn is from 2,000 to 10,000, preferably from 2,500 to 8,000. As the polyester resin D, a urea-modified polyester (UMPE) may be used, and may have urethane bonds and urea bonds. A molar ratio of a urea bond content to a urethane bond content is generally from 100/0 to 10/90, preferably from 80/20 to 20/80, more preferably from 60/40 to 30/70. When a molar

ratio of the urea bond is less than 10 %, the hot-offset resistance deteriorates.

[0096]

The urea-modified polyester (UMPE) is manufactured by publicly known methods, such as a one-shot process. A weight average molecular weight of the urea-modified polyester (UMPE) is generally 10,000 or more, preferably from 20,000 to 500,000, more preferably from 30,000 to 100,000. When a weight average molecular weight is less than 10,000, the hot-offset resistance deteriorates.

[0097]

In the present invention, the polyester resin (UMPE) modified by the urea bonds used when necessary may be used not only alone, but also in combination with an unmodified polyester resin (PE) contained as a toner binder component. The combined use with (PE) improves the low temperature fixing property and the glossiness for using in a full color apparatus, and is more preferable than a single use of (UMPE).

[0098]

Examples of (PE) include a condensation polymer of polyol (PO) having same component as the polyester component (UMPE) and polycarboxylic acid (PC), and the like, and a preferable molecular weight of PE is similar to the case of (UMPE). Further, (PE) may be not only unmodified polyester, but also modified with a chemical bond other than a urea bond, for example, with a urethane bond.

[0099]

Both of (UMPE) and (PE) are preferably at least partially compatible with each other in terms of the low temperature fixing property and the hot-offset resistance. Therefore, (UMPE) preferably has a polyester component similar to a polyester component of (PE). A weight ratio of (UMPE) to (PE) in a case of causing (PE) to be contained is generally from 5/95 to 80/20,

preferably from 5/95 to 30/70, more preferably from 5/95 to 25/75, and particularly preferably from 7/93 to 20/80. When a weight ratio of (UMPE) is less than 5 %, the hot-offset resistance deteriorates, both of the heat-resistant storage stability and the low temperature fixing property may not be satisfactorily satisfied.

[0100]

A hydroxyl value of (PE) is preferably 5 or more. An acid value (mg KOH/g) of (PE) is generally from 1 to 30, preferably from 5 to 20. The given acid value allows the toner to easily have negative electrostatic property and affinity of paper and toner improves in fixing to paper, and the low temperature fixing property improves. However, when an acid value exceeds 30, there is a deteriorating tendency in charge stability, especially in an environmental variation. A variation of an acid value in a polyaddition reaction between the prepolymer A and the amine B leads to a variation in a granulation step, and control in emulsification becomes difficult.

[0101]

In the toner of the present invention, the binder resin generally has a glass transition point (T<sub>g</sub>) of from 45 to 65 °C, preferably from 45 to 60 °C. When T<sub>g</sub> is less than 45 °C, heat resistance deteriorates, and when T<sub>g</sub> exceeds 65 °C, the low temperature fixing property becomes insufficient.

[0102]

As the coloring agent used in the present invention, all of publicly known dye and pigments may be used, including carbon black, nigrosine dye, iron black, Naphthol Yellow S, Hansa Yellow (10G, 5G, and G), cadmium yellow, yellow iron oxide, yellow ocher, chrome yellow, Titanium Yellow, Polyazo Yellow, Oil Yellow, Hansa Yellow (GR, A, RN, and R), Pigment Yellow L Benzidine Yellow (G and GR), Permanent Yellow (NCG), Vulcan Fast Yellow (5G and R), Tartrazine Lake, Quinoline Yellow Lake,

Anthragen Yellow BGL, isoindolinone yellow, red oxide, red lead oxide, red lead, cadmium red, cadmium mercury red, antimony vermilion, Permanent Red 4R, Para Red, Fire Red, p-chloro-o-nitroaniline red, Lithol Fast Scarlet G, Brilliant Fast Scarlet, Brilliant Carmine BS, Permanent Red (F2R, F4R, FRL, FRLl, and F4 RH), Fast Scarlet VD, Vulcan Fast Rubine B, Brilliant Scarlet G, Lithol Rubine GX, Permanent Red F5R, Brilliant Carmine 6B, Pigment Scarlet 3B, Bordeaux 5B, Toluidine Maroon, Permanent Bordeaux F2K, Helio Bordeaux BL, Bordeaux 10B, BON Maroon Light, BON Maroon Medium, eosine lake, Rhodamine Lake B, Rhodamine Lake Y, Alizarin Lake, Thioindigo Red B, Thioindigo Maroon, Oil Red, quinacridon red, Pyrazolone Red, Polyazo Red, Chromium Vermilion, Benzidine Orange, Perynone Orange, Oil Orange, cobalt blue, cerulean blue, Alkali Blue Lake, Peacock Blue Lake, Victoria Blue Lake, metal-free phthalocyanine blue, Phthalocyanine blue, Fast Sky Blue, Indanthrene Blue (RS and BC), indigo, ultramarine blue, iron blue, Anthraquinone Blue, Fast Violet B, Methyl Violet Lake, cobalt violet, manganese violet, dioxane violet, Anthraquinone Violet, chrome green, zinc green, chromium oxide, viridian emerald green, Pigment Green B, Naphthol Green B, Green Gold, Acid Green Lake, Malachite Green Lake, Phthalocyanine Green, Anthraquinone Green, titanium oxide, zinc white, lithopone, and mixtures thereof.

A content of the coloring agent is generally from 3 to 10 % by weight, preferably 1 to 15% by weight of the toner.

[0103]

The coloring agent used in the present invention may also be used as a masterbatch combined with the resin.

Examples of the binder resin used for manufacturing the masterbatch, or kneaded with the masterbatch include, in addition to the previously mentioned modified or unmodified polyester resin, styrene, such as polystyrene, poly-p-chlorostyrene, and polyvinyl toluene, and a polymer of the substitution product;

styrene copolymers, such as a styrene-p-chlorostyrene copolymer, a styrene-propylene copolymer, a styrene-vinyltoluene copolymer, a styrene-vinylnaphthalene copolymer, a styrene-methyl acrylate copolymer, a styrene-ethyl acrylate copolymer, a styrene-butyl acrylate copolymer, a styrene-octyl acrylic acid copolymer, a styrene-methyl methacrylate copolymer, a styrene-ethyl methacrylate copolymer, a styrene-butylmethacrylic acid copolymer, a styrene- $\alpha$ -methyl chloromethacrylate copolymer, a styrene-acrylonitrile copolymer, a styrene-vinyl methyl ketone copolymer, a styrene-butadiene copolymer, a styrene-isoprene copolymer, a styrene-acrylonitrile-indene copolymer, and a styrene-maleic acid copolymer and a styrene-maleic ester copolymer; polymethylmethacrylate, polybutyl methacrylate, polyvinyl chloride, polyvinyl acetate, polyethylene, polypropylene, polyester, epoxy resin, epoxy polyol resin, polyurethane, polyamide, polyvinyl butyral, polyacrylic resin, rosin, modified rosin, terpene resin, aliphatic or alicyclic hydrocarbon resin, aromatic petroleum resin, chlorinated paraffin, paraffin wax, and the like. Each of the resins may be used alone or in combination.

[0104]

The present masterbatch may be obtained by mixing and kneading resin for the masterbatch and a coloring agent under high shearing force. In the case, an organic solvent may be used for increasing interaction between the coloring agent and the resin. In addition, a flushing process is preferably used, in which aqueous paste containing water of the coloring agent is mixed and kneaded with the resin and an organic solvent to thereby transfer the coloring agent to a resin side, and then moisture and an organic solvent component are removed. According to the process, a wet cake of the coloring agent may be directly used. Accordingly, drying is not required and the process is preferably used. In mixing and kneading, a high-shear dispersing

device, such as a 3-roll mill, is preferably used.

[0105]

A releasing agent (wax) may also be contained in the toner of the present invention with the binder and the coloring agent. Publicly known wax may be used as wax, including, for example, polyolefin wax (polyethylene wax, polypropylene wax, and the like); long chain hydrocarbon (paraffin wax, Sasol wax, and the like); carbonyl group-containing wax, and the like. Among the wax, the carbonyl group-containing wax is preferable. Examples of the carbonyl group-containing wax include poly alkane acid ester (carnauba wax, montan wax, trimethylolpropane tribehenate, pentaerythritol tetrabehehenate, pentaerythritol diacetate dibehenate, glycerine tribehenate, 1,18-octadecanediol distearate, and the like); polyalkanol ester (tristearyltrimellitic acid, distearyl maleate, and the like); poly alkane acid amide (ethylenediamine dibehenyl amide, and the like); polyalkyl amide (trimellitic acid tristearylamide, and the like); and dialkyl ketone (distearyl ketone, and the like), and the like. The poly alkane acid ester is preferable among the carbonyl group-containing wax.

[0106]

The wax of the present invention generally has a melting point of from 40 to 160 °C, preferably from 50 to 120 °C, more preferably from 60 to 90 °C. Wax having a melting point less than 40 °C, has a bad influence on the heat-resistant storage stability, and wax having a melting point exceeding 160 °C easily causes cold offset in low temperature fixing. Melt viscosity of wax is preferably from 5 to 1,000 cps, more preferably from 10 to 100 cps as a measured value in a temperature higher than the melting point by 20 °C. Wax having melt viscosity exceeding 1,000 cps is insufficient in an improvement effect on the hot-offset resistance and the low temperature fixing property. A content of wax in the toner is generally from 0 to 40 % by weight,

preferably from 3 to 30 % by weight.

[0107]

Toner of the present invention may contain a charge control agent when necessary. All publicly known control agents may be used as the charge control agent, including, for example, nigrosine dye, triphenylmethane dye, chromium-containing metal complex dye, molybdic acid chelate pigment, rhodamine dye, alkoxyamine, quarternary ammonium salt (including fluorine-modified quarternary ammonium salt), alkylamide, simple substance or a compound of phosphorus, simple substance or a compound of tungsten, fluorine active agent, salicylic acid metallic salt, metallic salt of a salicylic acid derivative, and the like. Specifically, examples of the charge control agent include Bontron 03 of Nigrosine dye, Bontron P-51 of quarternary ammonium salt, Bontron S-34 of metal-containing azo dye, E-82 of metal complex of oxynaphthoic acid, E-84 of metal complex of salicylic acid, E-89 of the phenolic condensation product (made by Orient Chemical Industries Co., Ltd.), TP-302 and TP-415 of molybdenum complex of quarternary ammonium salt, (made by Hodogaya Chemical Co., Ltd.), COPY CHARGE PSY VP2038 of quarternary ammonium salt, COPY BLUE PR of triphenylmethane derivative, COPY CHARGE NEG VP2036 of quarternary ammonium salt, COPY CHARGE NX VP434 (made by Hoechst AG), LRA-901 and LR-147 being boron complex (made by Japan Carlit Co., Ltd.), copper phthalocyanine, perylene, quinacridon, and azo pigments, and a polymeric compound having a functional group, such as sulfonic group, carboxyl group, and quarternary ammonium salt.

[0108]

An amount of charge control agent used in the present invention is not specifically limited, and determined by a toner manufacturing method including a kind of the binder resin, presence or absence of additives used when necessary, and a dispersion method, and the like. The amount is preferably in a

range of from 0.1 to 10 parts by weight, preferably in a range of from 0.2 to 5 parts by weight relative to 100 parts by weight of binder resin. When the amount exceeds 10 parts by weight, the toner has an excessively high charge, effect of main electrification control agent is reduced, electrostatic attraction with a development roller increases, and fluidity lowering of a developer and lowering of image density are caused.

The charge control agents may be melted and kneaded with the masterbatch and the resin and then dissolved and dispersed, may be directly added to the organic solvent when being dissolved and dispersed, or may be fixed to the toner surface after toner particles are prepared.

[0109]

An external additive is preferably added to assist fluidity, developing property, and electrostatic property of toner particles obtained in the present invention. Inorganic fine particles may be preferably used as the external additive. Primary particle sizes of the inorganic fine particle are preferably from 5  $\mu\text{m}$  to 2  $\mu\text{m}$ , and particularly preferably from 5  $\mu\text{m}$  to 500  $\mu\text{m}$ . A specific surface area by a BET method is preferably from 20 to 500  $\text{m}^2/\text{g}$ . A using rate of the inorganic fine particles is preferably from 0.01 to 5 % by weight of toner, particularly preferably from 0.01 to 2.0 % by weight.

[0110]

Specific examples of the inorganic fine particles include silica, alumina, titanium oxide, barium titanate, magnesium titanate, calcium titanium, strontium titanate, zinc oxide, tin oxide, silica sand, clay, mica, wollastonite, diatomaceous earth, chromium oxide, cerium oxide, iron oxide red, antimony trioxide, magnesium oxide, zirconium oxide, barium sulfate, barium carbonate, calcium carbonate, silicon carbide, silicon nitride, and the like.

[0111]



Other examples of the external additive include polymeric particles, such as polystyrene or copolymer of methacrylic acid ester obtained by soap-free emulsion polymerization, suspension polymerization, or dispersion polymerization, silicon resin, benzoguanamine resin, nylon resin, or other polycondensed or thermosetting resins.

[0112]

Such external additives may treat surfaces, increase hydrophobicity, and prevent deterioration of flow characteristics or electrification properties even under high humidity. For example, a silane coupling agent, sililation reagent, silane coupling agent having a fluorinated alkyl group, organic titanate coupling agent, aluminum coupling agent, silicone oil, modified silicone oil, and the like are mentioned as a preferable surface treatment agents.

[0113]

Examples of cleanability improvers for removing the developer remaining on a photoconductor or a primary transfer medium after transfer include fatty acid metal salt, such as zinc stearate, calcium stearate, and stearin acid, polymer fine particles manufactured by soap-free emulsion polymerization, such as polymethylmethacrylate fine particles and polystyrene fine particles, and the like. The polymer fine particles have preferably relative narrow particle size distribution, and a volume average particle size of from 0.01 to 1  $\mu$ m.

[0114]

Next, a method of manufacturing the toner of the present invention is described in more detail.

In order to manufacture the toner of the present invention, first, an oily dispersion liquid being in a state where the isocyanate group-containing polyester prepolymer A is dissolved, the coloring agent is dispersed, and the releasing agent is dissolved or dispersed in an organic solvent is prepared.

The oily dispersion liquid is pulverized in a wet milling step for pulverizing and uniformly dispersing the coloring agent contained therein by using a wet milling device. In the case, the pulverization process time is approximately from 30 to 120 minutes.

[0115]

Next, in a dispersion (emulsification) step, the oily dispersion liquid thus obtained is dispersed in an aqueous medium under the presence of inorganic fine particles and/or polymer fine particles to form an oil-in-water type dispersion liquid (emulsified liquid). In the dispersion liquid, the isocyanate group-containing polyester prepolymer A is allowed to react with an amine B in the reaction step to produce a urea-modified polyester resin C having urea bonds.

[0116]

As the organic solvent, a solvent which is capable of dissolving the polyester resin and insoluble or slightly soluble in water is used. The boiling point is generally from 70 to 120 °C, preferably from 60 to 150 °C. Examples of such organic solvents include ethyl acetate, methyl ethyl ketone, and the like.

[0117]

In the present invention, the masterbatch color particles are preferably used as a coloring agent, whereby uniform dispersion of the coloring agent may be efficiently performed.

In the present invention, a polyester resin D being unreactive with the amine is preferably dissolved in the organic solvent as an auxiliary component. Further, the polyester resin D may also be dispersed in the aqueous medium.

[0118]

In the present invention, a dispersing device for dispersing the oily dispersion liquid in the aqueous medium is not particularly limited, and publicly known dispersion machines,

such as a low-speed shear type, high-speed shear type, friction type, high pressure jet type, ultrasonic type, and the like may be used. The high-speed shear type is preferred to obtain the dispersed particles having particle sizes of from 2 to 20  $\mu\text{m}$ .

5 When the high-speed shear type dispersion machine is used, revolution speed is not particularly limited, but is generally from 1,000 to 30,000 rpm, preferably from 5,000 to 20,000 rpm. Dispersion time is not particularly limited, but a batch method  
10 is generally from 0 to 150  $^{\circ}\text{C}$  (under pressure), preferably from 40 to 98  $^{\circ}\text{C}$ . A higher temperature is preferable because of low viscosity of the dispersion liquid and easy dispersion.

[0119]

An amount of the aqueous medium is generally from 50 to  
15 2,000 parts by weight, and preferably from 100 to 1,000 parts by weight relative to 100 parts by weight of toner solid contents, such as the prepolymer A, coloring agent, releasing agent, and polyester resin D which are contained in the oily dispersion liquid. When the amount is less than 50 parts by weight, a  
20 dispersion state of the toner solid content is unsatisfactory and the toner particles having a predetermined particle size may not be obtained. An amount exceeding 2,000 parts by weight is not economical. A dispersing agent may also be used when necessary. When the dispersing agent is used, particle size distribution is  
25 sharpened and dispersion is preferably stabilized.

Time until the oily liquid subjected to wet milling is dispersed in the aqueous medium after processing is preferably for a short time as much as possible.

[0120]

30 As the aqueous medium used in the present invention, water may be used alone or in combination with a solvent mixable with water. The mixable solvents include alcohol (methanol, isopropanol, ethylene glycol, and the like), dimethylformamide,

tetrahydrofuran, Cellosolve (methyl Cellosolve, and the like), and lower ketone (acetone, methyl ethyl ketone, and the like).

[0121]

In order to emulsify and disperse an oil phase containing the toner solid contents into a liquid (aqueous medium) containing water, various kinds of surfactants (emulsifiers) may be used as a dispersing agent. Such dispersing agents include an anionic surfactant, such as alkylbenzene sulfonate,  $\alpha$ -olefin sulfonate and phosphoric ester, amine salt type, such as alkylamine salt, amino alcohol fatty acid derivative, polyamine fatty acid derivative and imidazoline, quarternary ammonium salt type cationic surfactant, such as alkyl trimethylammonium salt, dialkyl dimethylammonium salt, alkyl dimethylbenzyl ammonium salt, pyridinium salt, alkyl isoquinolinium salt and benzethonium chloride, nonionic surfactant, such as fatty acid amide derivative and polyhydric alcohol derivative, and for example, amphoteric surfactant, such as alanine, dodecyl di(aminoethyl) glycine, di(octyl aminoethyl) glycine, N-alkyl-N, and N-dimethylammonium betaine.

[0122]

In the present invention, effect of the surfactants may be obtained in a small amount by using a surfactant having a fluoroalkyl group. Examples of preferably used anionic surfactants having the fluoroalkyl group include fluoroalkyl carboxylic acid having 2 to 10 carbon atoms and metallic salt thereof, perfluorooctanesulfonyl glutamate, 3-[omega fluoroalkyl (C6-C11) oxy]-1-alkyl (C3-C4) sodium sulfonate, 3-[omega fluoroalkanoyl (C6-C8)-N-ethylamino]-1-sodium propanesulfonate, fluoroalkyl (C11-C20) carboxylic acid and metallic salt thereof, perfluoroalkyl carboxylic acid (C7-C13) and metallic salt thereof, perfluoroalkyl (C4-C12) sulfonic acid and metallic salt thereof, perfluorooctane sulfonate diethanolamide, N-propyl-N-(2-hydroxyethyl) perfluorooctanesulfonamide,

perfluoroalkyl (C6-C10) sulfonamide propyl trimethylammonium salt, perfluoroalkyl (C6-C10)-N-ethylsulfonyl glycine salt, mono-perfluoroalkyl (C6-C16) ethyl phosphoric ester, and the like.

5 [0123]

Examples of trade names include SURFLON S-111, S-112 and S-113 (made by Asahi Glass Co., Ltd.), FLUORAD FC-93, FC-95, FC-98 and FC-129 (made by Sumitomo 3M Limited), UNIDYNE DS-101 and DS-102 (made by Daikin Industries, Ltd.), MEGAFAC F-110,  
10 F-120, F-113, F-191, F-812 and F-833 (made by Dainippon Ink & Chemicals, Incorporated), (EFTOP EF-102, 103, 104, 105, 112, 123A, 123B, 306A, 501, 201 and 204, (made by JEMCO Inc.), FTERGENT F-100 and F150 (made by Neos Co., Ltd.), and the like.

[0124]

15 Examples of the cationic surfactants include aliphatic primary, secondary and tertiary amine acid each having a fluoroalkyl group, aliphatic quarternary ammonium salt, such as perfluoroalkyl (C6-C10) sulfonamide propyl trimethylammonium salt, benzalkonium salt, benzethonium chloride, pyridinium salt,  
20 and imidazolinium salt. Examples of trade names include SURFLON S-121 (made by Asahi Glass Co., Ltd.), FLUORAD FC-135 (made by Sumitomo 3M Limited), UNIDYNE DS-202 (made by Daikin Industries, Ltd.), MEGAFACK F-150 and F-824 (made by Dainippon Ink & Chemicals, Incorporated), EFTOP EF-132 (made by JEMCO Inc.),  
25 FTERGENT F-300 (made by Neos Co., Ltd.), and the like.

[0125]

As the inorganic fine particles caused to be present in the aqueous medium, various kinds of conventionally known inorganic compounds which are insoluble or hardly soluble in water may be  
30 used. Examples of such inorganic compounds include tricalcium phosphate, calcium carbonate, titanium oxide, colloidal silica, hydroxyapatite, and the like.

As the polymer fine particles caused to be present in the

aqueous medium, various kinds of conventionally known polymer fine particles which are insoluble or hardly soluble in water may be used. Examples of such polymer fine particles include fine particles of hydrophobic polymers, such as hydrocarbon system resin, fluorine-containing resin, and silicone resin.

[0126]

The fine particles generally have particle sizes smaller than particle sizes of toner, and a value of a particle size ratio of [volume average particle size of fine particles]/[volume average particle size of toner] is preferably in a range of from 0.001 to 0.3 from a viewpoint of particle size uniformity. When the particle size ratio is greater than 0.3, since the fine particles may not adhere to the toner surface efficiently, resulting toner tends to have wide particle size distribution.

The volume average particle size of the fine particles may be suitably adjusted in the above range of particle size ratio such that the particle size becomes suitable for obtaining toner having a desired particle size. For example, to form toner having a volume average particle size of 5  $\mu\text{m}$ , the volume average particle size of the toner is preferably from 0.0025 to 1.5  $\mu\text{m}$ , particularly preferably from 0.005 to 1.0  $\mu\text{m}$ , and to form toner having a volume average particle size of 10  $\mu\text{m}$ , the volume average particle size of the toner is preferably from 0.005 to 3  $\mu\text{m}$ , particularly preferably from 0.05 to 2  $\mu\text{m}$ .

[0127]

In the present invention, various kinds of hydrophilic high polymers which form polymer protective colloid in the aqueous medium may be caused to be present in the aqueous medium as a dispersion stabilizer. Examples of monomer components forming such polymer substances are as follows.

Acid, such as acrylic acid, methacrylic acid,  $\alpha$ -cyanoacrylic acid,  $\alpha$ -cyanomethacrylic acid, itaconic acid,

crotonic acid, fumaric acid, maleic acid or maleic anhydride, or a hydroxyl group-containing (meta)acrylic monomer, For example,  $\beta$ -hydroxyethyl acrylate,  $\beta$ -hydroxyethyl methacrylate,  $\beta$ -hydroxypropyl acrylate,  $\beta$ -hydroxypropyl methacrylate,  $\gamma$ -hydroxypropyl acrylate,  $\gamma$ -hydroxypropyl methacrylate, 3-chloro-2-hydroxypropyl acrylate, 3-chloro-2-hydroxypropyl methacrylate, diethylene glycol monoacrylic ester, diethylene glycol monomethacrylic ester, glycerol monoacrylic ester, glycerol monomethacrylic ester, N-methylolacrylamide, N-methylolmethacrylamide, and the like, vinyl alcohol or ether with vinyl alcohol, for example, vinyl methyl ether, vinyl ethyl ether, vinyl propyl ether, and the like, or esters of vinyl alcohol and a carboxyl group-containing compound, for example, vinyl acetate, vinyl propionate, vinyl butyrate, and the like, acrylamide, methacrylamide, diacetone acrylamide, or methylol compound thereof, acid chloride, such as acryloyl chloride and methacryloyl chloride, vinyl monomer containing a nitrogen atom or heterocyclic ring thereof, such as vinylpyridine, vinylpyrrolidone, vinylimidazole, ethyleneimine, and the like.

[0128]

Examples of other polymer substances which may be preferably used in the present invention include a polyoxyethylene compound, such as polyoxyethylene, polyoxypropylene, polyoxyethylene alkylamine, polyoxypropylene alkylamine, polyoxyethylene alkylamide, polyoxypropylene alkylamide, polyoxyethylene nonylphenyl ether, polyoxyethylene lauryl phenyl ether, polyoxyethylene stearyl phenyl ester and polyoxyethylene nonylphenyl ester, and cellulose, such as methyl cellulose, hydroxyethyl cellulose and hydroxypropyl cellulose

[0129]

In the present invention, a method including a step of evaporating and removing an organic solvent by gradually increasing temperature of an entire system may be adopted to

remove a fluid medium contained in the emulsified dispersion liquid obtained after the polyaddition reaction between the prepolymer A and the amine B in a fluid medium removal step. Circularity of toner is controllable by intensity of liquid stirring before removing the organic solvent and removing time of the organic solvent. By slowly removing the solvent, a toner particle has a shape of 0.980 or more in terms of sphericity, and by vigorously stirring the emulsion and removing the solvent for a short time, a toner particle has a rugged or infinite shape of from 0.900 to 0.950 in terms of sphericity. The sphericity may be controlled in the range of from 0.850 to 0.990 by removing the solvent while stirring the emulsified liquid with powerful force in a stirring tank at from 30 to 50 °C during solvent removal after emulsification dispersion in the aqueous medium and reaction. Volumetric shrinkage is assumed to occur by rapidly removing the organic solvent contained, such as ethyl acetate, during granulation.

[0130]

As for the removal of the fluid medium, such a method may be adopted that the emulsified dispersion liquid is sprayed in a dry atmosphere and the organic solvent is thoroughly removed to form toner fine particles, and the water-based dispersing agent is removed by evaporation. A heated gas, such as air, nitrogen gas, carbon dioxide gas, and combustion gas, preferably various kinds of air currents heated at temperature equal to or higher than a boiling point of the fluid medium having a highest boiling point may be used as the dry atmosphere into which the emulsified dispersion liquid is sprayed. Quality toner may be obtained by brief processing by using a spray drier, belt dryer, rotary kiln, or the like.

Although time period between the reaction and the removal of the solvent after the reaction is preferably minimized, the time period is generally 25 hours or shorter.



[0131]

When calcium phosphate or the like which is soluble in acid or alkali is used as the inorganic fine particles, the inorganic fine particles may be removed from the toner particles by a method of washing the fine particles with acid, such as hydrochloric acid, after dissolving the inorganic fine particles, such as the calcium phosphate. Alternatively, the inorganic fine particles may be removed by using an enzymatic decomposition operation. When a dispersing agent is used, the dispersing agent may be allowed to remain on the surface of toner particles, but is preferably removed by washing after the reaction between the prepolymer A and the amine B for better toner charge ability.

[0132]

A solvent capable of dissolving the prepolymer and the urea modified polyester may be added in the aqueous medium to lower viscosity of the dispersion liquid after the reaction. The solvent is preferably used for sharpening particle size distribution. The solvent is preferably volatile and has a boiling point less than 100 °C from a viewpoint of easier removal. Such solvents include toluene, xylene, benzene, carbon tetrachloride, methylene chloride, 1,2-dichloroethane, 1,1,2-trichloroethane, trichloroethylene, chloroform, monochlorobenzene, dichloroethylidene, methyl acetate, ethyl acetate, methyl ethyl ketone, methyl isobutyl ketone, and the like. Each of the solvents may be used alone or in combination of two or more kinds. In particular, aromatic solvents, such as toluene and xylene, and halogenated hydrocarbon, such as methylene chloride, 1,2-dichloroethane, chloroform, and carbon tetra-chloride, are preferred. An amount of the solvent used is generally from 0 to 300 parts by weight, preferably from 0 to 100 parts by weight, and more preferably from 25 to 70 parts by weight relative to 100 part by weight of the prepolymer (A). When the solvent is used, the solvent is removed by heating under

normal pressure or reduced pressure after the reaction between the prepolymer A and the amine B.

[0133]

Reaction time between the prepolymer A and the amine B is selected depending on reactivity by a combination of an isocyanate group structure of the prepolymer (A) and the amine (B), and is generally from 10 minutes to 40 hours, preferably from 2 to 24 hours. Reaction temperature is generally from 0 to 150 °C, preferably from 40 to 98 °C. A publicly known catalyst may be used when necessary. Specifically, dibutyltin laurate, dioctyltin laurate, and the like are mentioned.

[0134]

When particle size distribution of the toner particles in the emulsified dispersion liquid after the reaction between the prepolymer A and the amine B is wide, and washing and drying processes are performed while the particle size distribution is maintained, the toner particles may be classified to adjust the toner particles in desired particle size distribution. In a classification operation in the case, fine particle portions may be removed by using a cyclone, decanter, centrifugal separation, or the like in the liquid. Although the classification operation may be performed after acquiring toner particles as powder after the drying, the classification operation is preferably performed in the liquid in terms of the efficiency. Obtained unnecessary fine particles or coarse particles may be again returned to the kneading step to be used for forming particles. In the case, the fine particles or coarse particles may be in a wet condition.

The used dispersing agent is preferably removed from the obtained dispersion liquid as much as possible, and preferably removed simultaneously with the classification operation.

[0135]

When the toner particles after drying are mixed with a different kind of particles, such as a releasing agent, charging

control agent and fluidizer, when necessary, mechanical impact force is applied to the mixed powder body, whereby the different kind of particles may be fixed and fused on toner particle surfaces, and desorption of the different kind of particles from the surfaces of obtained complex particles may be prevented.

As specific means, there are a method in which impact force is applied to the mixture by using a blade which rotates at high speed, a method in which the mixture is fed in a high-speed flow to cause the mixture to be accelerated, and cause the particles or the complex particles to collide with an appropriate collision plate, and the like. Examples of devices therefor include angmill (made by Hosokawa Micron Corporation), modified I-type mill (made by Nippon Pneumatic MFG., Co., Ltd.) having reduced pulverization air pressure, hybridization system (made by Nara Machine Corporation), Krypton System (made by Kawasaki Heavy Industries, Ltd.), automatic mortar, and the like.

[0136]

When the toner of the present invention is used for a two-component developer, the toner may be used by being mixed with a magnetic carrier. A content ratio of the toner to the carrier in the developer is preferably from 1 to 10 parts by weight relative to 100 parts by weight of the carrier. As a magnetic carrier, conventionally known carriers may be used, such as iron powder, ferrite powder, magnetite powder, and magnetic resin carrier having particle sizes of from approximately 20 to 200  $\mu\text{m}$ . Examples of coating materials include an amino resin, urea-formaldehyde resin, melamine resin, benzoguanamine resin, urea resin, polyamide resin, epoxy resin, and the like. Further, polyvinyl and polyvinylidene resins, for example, a polystyrene resin, such as acrylic resin, polymethyl methacrylate resin, polyacrylonitrile resin, polyvinyl acetate resin, polyvinyl alcohol resin, polyvinyl butyral resin, polystyrene resin, and styrene-acrylic copolymer resin, halogenated olefin resin, such

as polyvinyl chloride, polyester resin, such as polyethylene terephthalate resin and polybutylene terephthalate resin, polycarbonate resin, polyethylene resin, polyvinyl fluoride resin, polyvinylidene fluoride resin, polytrifluoroethylene resin, polyhexafluoropropylene resin, copolymer of vinylidene fluoride and acrylic monomer, copolymer of vinylidene fluoride and vinyl fluoride, fluoroterpolymer, such as terpolymer of tetrafluoroethylene, vinylidene fluoride and non-fluorinated monomer, and silicone resin, and the like may be used. Conductive powder and the like may be contained in the coating resin when necessary. Such conductive powder includes metal powder, carbon black, titanium oxide, tin oxide, zinc oxide, and the like. Such conductive powder has preferably an average particle size of 1  $\mu\text{m}$  or less. When the average particle diameter becomes greater than 1  $\mu\text{m}$ , control of the electric resistance becomes difficult.

Toner of the present invention may be used also as magnetic toner or nonmagnetic toner of the one-component system which does not use the carrier.

[0137]

[Examples]

In the following, the present invention is described according to examples, however the present invention is not limited to the examples. In the following, a part represents a part by weight. Table 1 shows toner used in each example.

[0138]

Synthesis of organic fine particle emulsion (manufacturing example 1)

To a reaction vessel equipped with a stirring rod for synthesizing an organic fine particle emulsion and a thermometer, 683 parts of water, 11 parts of sodium salt of sulfuric acid ester of ethylene oxide adduct of methacrylic acid (ELEMNOL RS-30, made by Sanyo Chemical Industries, Ltd.), 83 parts of styrene, 83 parts of methacrylic acid, 110 parts of butyl

acrylate, and 1 part of ammonium persulfate were fed and stirred at 400 rpm for 15 minutes to obtain a white emulsion. The reaction vessel was heated to an inner temperature of 75 °C and followed by a reaction for 5 hours. The reaction mixture was further treated with 30 parts of 1 % aqueous solution of ammonium persulfate, aged at 75 °C for 5 hours, and an aqueous dispersion [fine particle dispersion 1] of a vinyl resin (copolymer of styrene-methacrylic acid-butyl acrylate sodium salt of sulfuric acid ester of ethylene oxide adduct of methacrylic acid) was obtained. A volume average particle size of the [fine particle dispersion 1] measured with LA-920 was 105 nm. Part of [fine particle dispersions 1] was dried to isolate a resin component. The resin component had a Tg of 59 °C, and a weight average molecular weight of 150,000.

[0139]

Adjustment of aqueous phase (manufacturing example 2)

A total of 990 parts of water, 99 parts of [fine particle dispersion 1], 35 parts of 48.5 % aqueous solution of sodium dodecyl diphenyl ether disulfonate, and 70 parts of ethyl acetate was mixed and stirred to obtain a milky liquid. The milky liquid is used as an [aqueous phase 1].

[0140]

Synthesis of low-molecular weight polyester (manufacturing example 3)

In a reaction vessel equipped with a cooling tube, a stirrer and a nitrogen gas feed tube, 229 parts of ethylene oxide 2 mole adduct of bisphenol A, 529 parts of propylene oxide 3 mole adduct of bisphenol A, 208 parts of terephthalic acid, 46 parts of adipic acid, and 2 parts of dibutyltin oxides were placed and reacted at 230 °C at normal pressure for 8 hours. The mixture was further reacted at reduced pressure of 10 to 15 mmHg for 5 hours, and then 44 parts of trimellitic anhydride is fed to the reaction vessel. The reaction mixture was further reacted at 180 °C at

normal pressure for 1.8 hours to obtain a [low-molecular weight polyester 1]. The [Low-molecular weight polyester 1] had a number average molecular weight of 2,500, a weight average molecular weight of 6,700, a peak molecular weight of 5,000, a Tg of 43 °C, and an acid value of 25.

[0141]

Synthesis of intermediate polyester (manufacturing example 4)

In a reaction vessel equipped with a cooling tube, a stirrer and nitrogen gas feed tube, 682 parts of ethylene oxide 2 mol adduct of bisphenol A, 81 parts of propylene oxide 2 mole adduct of bisphenol A, 283 parts of terephthalic acids, 22 parts of trimellitic anhydride, and 2 parts of dibutyltin oxide were placed and reacted at 230 °C at normal pressure for 8 hours, and further reacted under reduced pressure of 10 to 15 mmHg for 5 hours to obtain an [Intermediate polyester 1]. The [Intermediate polyester 1] had a number average molecular weight of 2,100, a weight average molecular weight of 9,500, a Tg of 55 °C, an acid value of 0.5, and a hydroxyl value of 51.

Next, 410 parts of [intermediate polyester 1], 89 parts of isophorone diisocyanate, and 500 parts of ethyl acetate were fed in a reaction vessel equipped with a cooling tube, a stirrer and a nitrogen gas feed tube, and reacted at 100 °C for 5 hours to obtain a [prepolymer 1]. The [prepolymer 1] had a free isocyanate content of 1.53 % by weight.

[0142]

Synthesis of ketimine (manufacturing example 5)

In a reaction vessel equipped with a stirring rod and a thermometer, 170 parts of isophoronediamine and 75 parts of methyl ethyl ketone were fed, and reacted at 50 °C for 5 hours to obtain a [ketimine compound 1]. An amine value of [ketimine compound 1] was 418.

[0143]

Synthesis of MB (manufacturing example 6)

A total of 1200 parts of water, 540 parts of carbon black (Printex 35, made by Degussa AG) [DBP oil absorption = 42 ml/100 mg, pH = 9.5], 1,200 parts of polyester resin was added and mixed in a Henschel mixer (made by Mitsui Mining Co., Ltd.). The  
5 mixture was kneaded for 30 minutes at 150 °C by using 2 rolls, and then cold-rolled and pulverized in a pulverizer to obtain [masterbatch 1].

[0144]

Preparation of oil phase (manufacturing example 7)

10 In a vessel equipped with a stirring rod and a thermometer, 378 parts of [low-molecular weight polyester 1], 110 parts of carnauba wax, 22 parts of CCA (salicylic acid metal zinc salt E-84: Made by Orient Chemical Industries, Ltd.), and 947 parts of ethyl acetate were fed and heated to 80 °C under stirring, held at  
15 80 °C for 5 hours, and then cooled to 30 °C over 1 hour. Next, 500 parts of [masterbatch 1] and 500 parts of ethyl acetate were fed in the vessel and mixed for 1 hour to obtain a [material solution 1].

Next, 1,324 parts of [Material solution 1] was shifted to a  
20 vessel, and carbon black and wax were dispersed by using a bead mill (ULTRAVISCO MILL, made by Aimex Co., Ltd.) at a liquid feed rate of 1 kg/hr, disc peripheral velocity of 6 m/second, using zirconia beads of 0.5 mm in diameter filled 80 % by volume and three paths. Next, 1,324 parts of 65 % ethyl acetate solution of  
25 [low-molecular weight polyester 1] was added, and the mixture was dispersed by one pass by the bead mill under the above conditions to obtain a [pigment-wax dispersion liquid 1]. Solid concentration (at 130 °C for 30 minutes) of the [pigment-wax dispersion liquid 1] was 50 %.

30 [0145]

[Example 1]

In a vessel, 115 parts of [Pigment-wax dispersion liquid 1], 749 parts of [prepolymer 1], and 2.9 parts of [ketimine compound

1] were fed and mixed at 5,000 rpm for 1 minute in a TK homo mixer (made by Tokushu Kika Kogyo Co., Ltd.), and then 1,200 parts of [Aqueous phase 1] were added to the vessel and mixed at a revolution speed of 12,500 rpm for 30 minutes in the TK homo mixer to obtain [emulsion slurry 1].

In a vessel equipped with a stirrer and a thermometer, the [emulsion slurry 1] is fed and heated at 35 °C for 7 hours to remove the solvent, aged at 45 °C for 4 hours to obtain [dispersion slurry 1].

10 [0146]

Next, 100 parts of [dispersion slurry 1] was filtered under reduced pressure, and then

(1): 100 parts of ion exchange water was added to the resultant filter cake and mixed in a TK homo mixer (at 12,000 rpm for 10 minutes), and then filtered.

(2): To the filter cake prepared in (1), 100 parts of 10 % aqueous sodium hydroxide were added and mixed in a TK homo mixer (at 12,000 rpm for 30 minutes), and then filtered under reduced pressure.

20 (3): To the filter cake prepared in (2), 100 parts of 10 % hydrochloric acid were added and mixed in a TK homo mixer (at 12,000 rpm for 10 minutes), and then filtered.

(4): To the filter cake prepared in (3), 300 parts of ion exchange water were added and mixed in a TK homo mixer (at 12,000 rpm for 10 minutes), and then a filtering operation was performed twice to obtain a [filter cake 1].

The [filter cake 1] was dried at 45°C for 48 hours in a circulating air dryer, and sieved with a 75- $\mu$ m mesh sieve to obtain [toner 1]. The present toner had a volume average particle size of 4.8  $\mu$ m, and a number average particle size of 3.9  $\mu$ m.

30 [0147]

Next, 100 parts of [toner 1] and 0.7 part of hydrophobic titanium oxide were mixed in a Henschel mixer, and completed



toner preparation.

[0148]

Synthesis of organic fine particle emulsion (manufacturing example 8)

5 In a reaction vessel equipped with a stirring rod and a thermometer, 683 parts of water, 11 parts of sodium salt of sulfuric acid ester of ethylene oxide adduct of methacrylic acid (ELEMNOL RS-30, made by Sanyo Chemical Industries, Ltd.), 80 parts of styrene, 83 parts of methacrylic acid, 110 parts of butyl acrylate, 12 parts of butyl thioglycolate, and 1 part of ammonium persulfate was fed and stirred for 15 minutes at 400 rpm to obtain a white emulsion. The emulsion was heated to an inner temperature of 75 °C and reacted for 5 hours. Further, 30 parts of 1 % aqueous solution of ammonium persulfate was added and the reaction mixture was aged at 75 °C for 5 hours to obtain an aqueous dispersion [fine particle dispersion 2] of a vinyl resin (copolymer of styrene-methacrylic acid-butyl acrylate-sodium salt of sulfuric acid ester of ethylene oxide adduct of methacrylic acid). The volume average particle size of the [fine particle dispersion 2] measured with LA-920 was 120 nm. Part of [fine particle dispersions 2] was dried to isolate a resin component. The resin component had a Tg of 42 °C, and a weight average molecular weight of 30,000.

[0149]

25 [Example 2]

[Toner 2] was obtained similar to Example 1, except that the [fine particle dispersion 2] was used instead of the [fine particle dispersion 1] in Example 1.

[0150]

30 Synthesis of organic fine particle emulsion (manufacturing example 9).

In a reaction vessel equipped with a stirring rod and a thermometer, 683 parts of water, 11 parts of sodium salt of

sulfuric acid ester of ethylene oxide adduct methacrylic acid (ELEMNOL RS-30, made Sanyo Chemical Industries, Ltd.), 103 parts of styrene, 83 parts of methacrylic acids, 90 parts of butyl acrylate, 12 parts of butyl thioglycolate, and 1 part of ammonium persulfate were fed and stirred for 15 minutes at 400 rpm to obtain a white emulsion. The emulsion was heated to an inner temperature of 75 °C and reacted for 5 hours. Further, 30 parts of 1 % aqueous solution of ammonium persulfate were added and the reaction mixture was aged at 75°C for 5 hours to obtain an aqueous dispersion [fine particle dispersion 3] of a vinyl resin (copolymer of styrene-methacrylic acid-butyl acrylate-sodium salt of sulfuric acid ester of ethylene oxide adduct of methacrylic acid). A volume average particle size of the [fine particle dispersion 3] measured with LA-920 was 110 nm. Part of [fine particle dispersions 3] was dried to isolate a resin component. The resin component had a Tg of 78 °C and a weight average molecular weight was 25,000.

[0151]

[Example 3]

[Toner 3] was obtained similar to Example 1, except that the [fine particle dispersion 3] was use instead of the [fine particle dispersion 1] in Example 1.

[0152]

Synthesis of organic fine particle emulsion (manufacturing example 10)

In a reaction vessel equipped with a stirring rod and a thermometer, 683 parts of water, 11 parts of sodium salt of sulfuric acid ester of ethylene oxide adduct of methacrylic acid (ELEMNOL RS-30, made by Sanyo Chemical Industries, Ltd.), 78 parts of styrene, 83 parts of methacrylic acid, 115 parts of butyl acrylate, 2 parts of butyl thioglycolate, and 1 part of ammonium persulfate were fed and stirred for 15 minutes at 400 rpm to obtain a white emulsion. The emulsion was heated to an

inner temperature of 75 °C and reacted for 5 hours. Further, 30 parts of 1 % aqueous solutions of ammonium persulfate was added, and the reaction mixture was aged at 75 °C for 5 hours to obtain an aqueous dispersion [fine particle dispersion 4] of a vinyl resin (copolymer of styrene-methacrylic acid-butyl acrylate-sodium salt of sulfuric acid ester of ethylene oxide adduct of methacrylic acid). A volume average particle size of [fine particle dispersion 4] measured with LA-920 was 115 μm. Part of [fine particle dispersions 4] was dried to isolate a resin component. The resin component had a Tg of 51 , and a weight average molecular weight of 100,000.

[0153]

[Example 4]

[Toner 4] was obtained similar to Example 1, except that the [Fine particle dispersion 4] was used instead of the [fine particle dispersion 1] in Example 1, and hydrophobic silica was used as an external additive instead of the hydrophobic titanium oxide.

[0154]

Synthesis of organic fine particle emulsion (manufacturing example 11)

In a reaction vessel equipped with a stirring rod and a thermometer, 683 parts of water, 11 parts of sodium salt of sulfuric acid ester of ethylene oxide adduct of methacrylic acid (ELEMNOL RS-30, made by Sanyo Chemical Industries, Ltd.), 68 parts of styrene, 93 parts of methacrylic acid, 115 parts of butyl acrylate, and 1 part of ammonium persulfate were fed and stirred at 400 rpm for 15 minutes to obtain a white emulsion. The emulsion was heated to an inner temperature of 75 °C and reacted for 5 hours. Further, 30 parts of 1 % aqueous solution of ammonium persulfate were added, and the reaction mixture was aged at 75 °C for 5 hours to obtain an aqueous dispersion [fine particle dispersion 5] of a vinyl resin (copolymer of

styrene-methacrylic acid-butyl acrylate-sodium salt of sulfuric acid ester of ethylene oxide adduct of methacrylic acid). A volume average particle size of the [fine particle dispersion 5] measured with LA-920 was 90 nm. Part of [fine particle dispersions 5] was dried to isolate a resin component. The resin component had a Tg of 56 °C and a weight average molecular weight of 150,000.

[0155]

Preparation of oil phase (manufacturing example 7-2)

10 A [material solution 2] was obtained similar to manufacturing example 7, except that 22 parts of CCA (salicylic acid metal complex E-84: Orient Chemical Industries, Ltd.) were not used in manufacturing example 7.

15 Next, 1,324 parts of [material solution 2] were shifted to a vessel and carbon black and wax were dispersed by using a bead mill (ULTRAVISCO MILL, made by Aimex Co., Ltd.) at a liquid feed rate of 1 kg/hr, disc peripheral velocity of 6 m/sec, using zirconia beads of 0.5 mm in diameter filled 80 % by volume and by three paths. Next, 1,324 parts of 65 % ethyl acetate solution of 20 [low-molecular weight polyester 1] was added, and the mixture was dispersed by one pass by using the bead mill under the above conditions to obtain a [pigment-wax dispersion liquid 2]. The solid concentration (130 °C for 30 minutes) of [pigment-wax dispersion liquid 2] was 50 %.

25 [0156]

[Example 5]

.. [Toner 5] was obtained similar to Example 1, except that the [fine particle dispersion 5] and the [pigment-wax dispersion liquid 2] were used instead of the [fine particle dispersion 1] and the [pigment-wax dispersion liquid 1] in Example 1, 30 respectively.

Next, 100 parts of the present toner and 0.5 part by weight of CCA (salicylic acid metal complex E-84: made by Orient

Chemical Industries, Ltd.) were mixed at 1,000 rpm by using a Henschel mixer, and further mixed at 6,000rpm in a Q type mixer (made by Mitsui Mining Co., Ltd.) to cause the CCA to fix to a toner surface. Preparation of [toner 5] was completed similar to  
5 Example 1, except that the hydrophobic silica was used as the external additive instead of the hydrophobic titanium oxide.

[0157]

Preparation of emulsion slurry (manufacturing example 12)

In a vessel, 753 parts of [Pigment-wax dispersion liquid 1],  
10 154 parts of [prepolymer 1], and 3.8 parts of [ketimine compound 1] are placed and mixed at 5,000 rpm for 1 minute in a TK homo mixer (made by Tokushu Kika Kogyo Co., Ltd.). Next, 1,200 parts of [Aqueous phase 1] was added to the vessel, and the mixture was mixed at 13,000 rpm for 20 minutes in a TK homo mixer to obtain  
15 [emulsion slurry 6].

[0158]

[Example 6]

[Toner 6] was obtained similar to Example 1, except that the [emulsion slurry 6] was used instead of [emulsion slurry 2] in  
20 Example 1. In a middle of solvent removal, a sample was shifted to a TK homo mixer and stirred at 12,500 rpm for 40 minutes to form the toner in an irregular shape.

[0159]

Synthesis of low-molecular weight polyester (manufacturing  
25 example 13)

In a reaction vessel equipped with a cooling tube, a stirrer and a nitrogen gas feed tube, 196 parts of propylene oxide 2 mole adduct of bisphenol A, 553 parts of ethylene oxide 2 mole adducts of bisphenol A, 210 parts of terephthalic acid, 79 parts of  
30 adipic acid and 2 parts of dibutyltin oxides are placed and reacted at 230 °C at normal pressure for 8 hours, and then reacted under a reduced pressure of 10 to 15 mmHg for 5 hours. Next, 26 parts of trimellitic anhydride was added to the reaction vessel,

and reacted at 180 °C and at normal pressure for 2 hours to obtain [low-molecular weight polyester 2].

The [Low-molecular weight polyester 2] had a number average molecular weight of 2,400, a weight average molecular weight of 6,200, a peak molecular weight of 5,200, a Tg of 43 °C, and an acid value 15.

[0160]

[Example 7]

[Toner 7] was obtained similar to Example 5, except that the [low-molecular weight polyester 2] was used instead of the [low-molecular weight polyester 1] in Example 5. In a middle of solvent removal, a sample was shifted to a TK homo mixer, and stirred at 13,000 rpm for 30 minutes to form toner in an irregular shape, whereby spindle-shaped toner was obtained.

[0161]

Adjustment of the aqueous phase (manufacturing example 14)

A total of 990 parts of water, 62 parts of [fine particle dispersion 1], 37 parts of 48.5 % aqueous solution of sodium dodecyl diphenyl ether disulfonate (ELEMNOL MON-7: made by Sanyo Chemical Industries, Ltd.), and 90 parts of ethyl acetate was mixed and stirred to obtain a milky liquid. The milky liquid was used as an [aqueous phase 6].

[0162]

[Comparative example 1]

[Toner 8] was obtained similar to Example 1, except that the [aqueous phase 6] was used instead of the [aqueous phase 1] in Example 1.

[0163]

Adjustment of the aqueous phase (manufacturing example 15)

A total of 990 parts of water, 77 parts of [fine particle dispersion 1], 37 parts of 48.5 % aqueous solution of sodium dodecyl diphenyl ether disulfonate (ELEMNOL MON-7: made by Sanyo Chemical Industries, Ltd.), and 90 parts of ethyl acetate was

mixed and stirred to obtain a milky liquid. The milky liquid was used as an [aqueous phase 7].

[0164]

[Comparative example 2]

5 [Toner 9] was obtained similar to Example 1, except that the [aqueous phase 7] was used instead of the [aqueous phase 1] in Example 1.

[0165]

10 In a reaction vessel equipped with a stirring rod and a thermometer, 683 parts of water, 11 parts of sodium salt of sulfuric acid ester of ethylene oxide adduct of methacrylic acid (ELEMNOL RS-30: made by Sanyo Chemical Industries, Ltd.), 138 parts of styrene, 138 parts of methacrylic acid, and 1 part of ammonium persulfate are fed and stirred for 15 minutes at 400 rpm  
15 to obtain a white emulsion. The emulsion was heated to an inner temperature of 75 °C and reacted for 5 hours. Further, 30 parts of 1 % aqueous solution of ammonium persulfate were added, and the mixture was aged at 75 °C for 5 hours to obtain an aqueous dispersion [fine particle dispersion 6] of a vinyl resin  
20 (copolymer of styrene-methacrylic acid-butyl acrylate-sodium salt of sulfuric acid ester of ethylene oxide adduct of methacrylic acid).

A volume average particle size of [fine particle dispersion 6] measured with LA-920 was 140 nm. Part of [fine particle  
25 dispersions 6] was dried to isolate a resin component. The resin component had a Tg of 152 °C, and a weight average molecular weight of 400,000.

[0166]

[Comparative example 3]

30 [Toner 10] was obtained similar to Example 1, except that the [fine particle dispersion 6] was used instead of the [fine particle dispersion 1] in Example 1. In a middle of solvent removal, a sample was shifted to a TK homo mixer, and stirred at

13,000 rpm for 30 minutes to form toner in an irregular shape.

[0167]

Synthesis of organic fine particle emulsion (manufacturing example 17)

5 In a reaction vessel equipped with a stirring rod and a thermometer, 683 parts of water, 11 parts of sodium salt of sulfuric acid ester of ethylene oxide adduct of methacrylic acid (ELEMNOL RS-30, made by Sanyo Chemical Industries, Ltd.), 63 parts of styrene, 83 parts of methacrylic acid, 130 parts of butyl acrylate, 12 parts of butyl thioglycolate, 1 part of ammonium persulfate were fed and stirred at 400 rpm for 15 minutes to obtain a white emulsion. The emulsion was heated to an inner temperature of 75 °C for 5 hours. Further, 30 parts of 1 % aqueous solution of ammonium persulfate were added, and the mixture was aged at 75 °C for 5 hours to obtain an aqueous dispersion [fine particle dispersion 7] of a vinyl resin (copolymer of styrene-methacrylic acid-butyl acrylate-sodium salt of sulfuric acid ester of ethylene oxide adduct of methacrylic acid).

[0168]

20 A volume average particle size of [fine particle dispersion 7] measured with LA-920 was 130 nm. Part of [fine particle dispersions 7] was dried to isolate a resin component. The resin component had a Tg of 30 °C, and a weight average molecular weight of 5,000.

25 [0169]

[Comparative example 4]

[Toner 11] was obtained similar to Example 1, except that the [fine particle dispersion 7] was used instead of the [fine particle dispersion 1] in Example 1.

30 Next, 100 parts of obtained toner and 0.7 part of hydrophobic silica were mixed in a Henschel mixer. Values of physical properties of the obtained toner were shown in Table 1.

[0170]



[Comparative example 5]

Binder resin 1 (Polyester resin: THF-insoluble component 0 wt%) 80 parts

5 Binder resin 2 (urea-modified polyester resin: THF-insoluble component 10 wt%) 20 parts

Wax (carnauba wax) 5 parts

Charge controlling agent (zinc complex of salicylic acid, Bontron E-84: made by Orient Chemical Industries, Ltd.)

2 parts

10 Coloring agent: carbon black (Printex35: made by Degussa) 10 parts

The above materials were sufficiently mixed in a blender, and then melted and kneaded with a two-roll mill heated at from 110 to 120 °C. The kneaded product was left to cool, roughly  
15 pulverized with a cutter mill, further pulverized with a pulverizing mill using a jet stream, and then toner particles were obtained by using an air classification device. The toner particles were transformed to spherical particles by using a surface treatment device (Suffusing System unit: made by Nippon  
20 Pneumatic Mfg. Co., Ltd.).

Further, 100 parts of present toner particles and 0.7 part of hydrophobic silica as an external additive were mixed in a Henschel mixer to obtain toner 12.

[0171]

25 The THF-insoluble content was measured according to a following method.

Approximately 1.0 g (A) of a sample resin or toner is precisely weighed.

Next, approximately 50 g of TFT is added to the sample,  
30 stirred and dissolved, then subjected to centrifugal separation, and left to stand at 20 °C for 24 hours. Insoluble contents are separated by using a glass filter.

The solvent was removed from the filtrate by drying in

vacuo, and a residual amount (B) of resin component was measured. The residual amount is an amount of THF-soluble components. The THF-insoluble content (%) is determined according to a following equation.

5           THF-insoluble content (%) =  $(A - B)/A$   
            [0172]

Table 1 shows physical properties determined as described above.

10           A developer containing 5 % by weight of toner and 95 % by weight of copper-zinc ferrite carrier having an average particle size of 40  $\mu$ m and being coated with a silicone resin was prepared. Then, by using Ricoh imagio Neo 450 capable of printing 45 A4-sized sheets per minute, continuous printing was performed, and evaluations were made on following criteria. Table 2 shows  
15           the results.

            [0173]

[Measurement method of quality characteristics]

            Quality characteristic measurement was performed as follows. Characteristic evaluation of following (1) to (3) was made by  
20           using belt fixing shown in Fig. 1 under following conditions.

            Belt tension: 1.5 kg/piece,

            Belt speed: 170 mm/sec,

            Fixation nip width: 10 mm,

            Fixing roller: (roller diameter:  $\Phi$  38 mm, surface material  
25           and hardness: foamed silicon having approximately 30 degrees (Asker C hardness)),

            Pressure roller: (roller diameter:  $\Phi$  50 mm, surface material and hardness: PFA tube + silicone rubber having a thickness of 1 mm and approximately 75 degrees (Asker C hardness)),

30           Diameter of metallic core:  $\Phi$  48 mm (iron having a wall thickness of 1mm),

            Heating roller: (roller diameter:  $\Phi$  30 mm) (aluminum having a wall thickness of 2 mm), and

Fixing belt: (diameter of belt:  $\Phi$  60 mm, base: nickel having a thickness of approximately 40  $\mu$ m, Releasing layer: silicone rubber of approximately 150  $\mu$ m, belt width: 310 mm).

[0174]

5 (1) Lowest fixing temperature

A copying test of an image was carried out by using a device equipped with the above belt fixing unit, and using a color copier Preter 550 made by Ricoh Company Limited in which Type 6200 paper made by Ricoh Company Limited was set. A lowest fixing  
10 temperature was defined as a fixing roll temperature at which a residual ratio of image density after rubbing a fixed image with a pat was 70 % or more.

[0175]

(2) Hot offset non-occurring temperature range

15 A color copier Preter 550 made by Ricoh Company Limited was used and adjusted such that monochromatic solid images of yellow, magenta, cyan and black, and intermediate-color solid images of red, blue and green are developed on transfer paper (Type 6000-70W made by Ricoh Company Limited) by using toner in an  
20 amount of  $1.0 \pm 0.1$  mg/cm<sup>2</sup> in a single color. In the belt fixing device shown in Fig. 1 (under the described conditions), temperature of the fixing belt is adjusted to be variable, and temperature at which offset does not occur was measured.

[0176]

25 (3) Glossiness

In the above monochromatic image sample, glossiness of the sample when fixing belt surface temperature is 160 °C was measured at an incident angle of 60 degrees by using a glossmeter made by Nippon Denshoku Industries Co., Ltd. Glossiness increases when a  
30 value of glossiness is higher. As a full color copy image, appropriate gloss of approximately 10 to 30 % is preferred.

[0177]

[Table 1]

Characteristics and construction of toner												
	Weight average particle size (Dv)	Number average particle size (Dn)	Dv/Dn	SF-1	Particles with SF-1 of 160 or more	Particles with SF-1 of 150 or more	Particle size of dispersed releasing agent	Dispersed particles of releasing agent	G' (80 °C)	G' (180 °C)	Maximum tanδ (80 to 130 °C)	Preparation method.
	μm	μm			(%)	(%)	μm					
Example 1	4.8	3.9	1.23	107	1.2	4.3	88	Concentrated in the vicinity of surface	1.2 X 106	2.1 X 103	3.5	Wet granulation
Example 2	5.8	4.8	1.21	118	1.5	6.2	95	Concentrated in the vicinity of surface	1.3 X 106	2.2 X 103	3.6	Wet granulation
Example 3	6.8	6.3	1.08	125	1.5	7.7	94	Concentrated in the vicinity of surface	1.4 X 106	2.3 X 103	4	Wet granulation
Example 4	6.3	5.3	1.19	130	3.5	8.8	88	Concentrated in the vicinity of surface	1.1 X 106	2.1 X 103	3.2	Wet granulation
Example 5	3.5	3.0	1.17	116	0.4	3.2	96	Concentrated in the vicinity of surface	6.5 X 105	6.7 X 102	7.3	Wet granulation
Example 6	5.3	4.5	1.18	139	4.8	10.5	95	Concentrated in the vicinity of surface	4.5 X 106	3.3 X 103	2.2	Wet granulation
Example 7	3.9	3.4	1.15	155	8.7	28.5	76	Concentrated in the vicinity of surface	5.8 X 107	7.8 X 103	1.9	Wet granulation
Comp. Ex. 1	7.2	5.9	1.22	125	2.2	5.5	85	Uniformly dispersed in toner	1.1 X 106	2.5 X 103	3.1	Wet granulation
Comp. Ex. 2	5.7	4.3	1.33	118	1.9	8.8	88	Uniformly dispersed in toner	1.3 X 106	2.1 X 103	2.8	Wet granulation
Comp Ex. 3	6.2	5.2	1.19	165	54.9	82.3	77	Concentrated in toner	1.0 X 106	2.0 X 103	4.5	Wet granulation
Comp. Ex. 4	2.8	2.3	1.22	125	3.5	9.0	75	Exposed from surface	6.2 X 105	6.1 X 102	6.6	Wet granulation
Comp. Ex. 5	6.5	4.8	1.35	120	3.2	7.8	65	Exposed from surface	5.8 X 107	7.8 X 103	5.1	Spherical product of pulverized toner

[0178]

[Table 2]

	Evaluation results of quality characteristics			Overall determination
	Lowest fixing temperature	Hot-offset occurring temperature	Glossiness	
	°C	°C	%	
Example 1	120	220 or more	22	○
Example 2	120	220 or more	25	○
Example 3	115	220 or more	26	○
Example 4	120	220 or more	20	○
Example 5	110	220 or more	27	○
Example 6	120	220 or more	21	○
Example 7	125	220 or more	18	○
Comp. Ex. 1	140	200	7	×
Comp. Ex. 2	140	200	6	×
Comp. Ex. 3	145	195	4	×
Comp. Ex. 4	155	220 or more	3	×
Comp. Ex. 5	145	220 or more	5	×

[0179]

[Effects of the Invention]

(1) According to the inventions of claims 1 and 16, in an image forming method using a fixing method for heating and fixing a toner image on a recording medium by a heating element, and one or more heating media heated by the heating element and a pressure member for causing the recording medium to be in press contact with one of the heating media, at least one of the heating media is a belt-shaped heating medium used by being applied with a fixed amount of oil or no oil on a belt, and toner containing at least a binder resin and a releasing agent as main components is used, wherein the toner has a weight average particle size of from 3.0 to 7.0  $\mu\text{m}$ , particle size distribution of  $1.00 \leq D_v/D_n \leq 1.25$  ( $D_v$ : weight average particle size,  $D_n$ : number average particle size) and an average value of a shape factor SF-1 of from 100 to 150, and contains toner particles

having SF-1 of 160 or more in an amount of 10 % by number or less, whereby an image forming method and an apparatus satisfying a low temperature fixing property and high releasability are obtained.

[0180]

(2) According to the inventions of claims 2 and 17, an image forming method and an apparatus satisfying the low temperature fixing property and the high releasability are obtained by using toner having a weight average particle size of from 3.0 to 5.0  $\mu\text{m}$ .

[0181]

(3) According to the inventions of claims 3 and 18, an image forming method and an apparatus satisfying the low temperature fixing property and the high releasability are obtained by using toner having particle size distribution of  $1.00 \leq D_v/D_n \leq 1.20$  (Dv: weight average particle size, Dn: number average particle size).

[0182]

(4) According to the inventions of claims 4 and 19, an image forming method and an apparatus satisfying the low temperature fixing property are obtained by using toner having an average shape factor SF-1 of from 100 to 130.

[0183]

(5) According to the inventions of claims 5 and 20, an image forming method and an apparatus satisfying the low temperature fixing property are obtained by using toner containing toner particles having a shape factor SF-1 of 150 or more in an amount of 10 % by number or less.

[0184]

(6) According to the inventions of claims 6, 7, 21 and 22, an image forming method and an apparatus satisfying dot reproducibility are obtained by using spindle-shaped toner.

[0185]

(7) According to the inventions of claims 8 and 23, an image forming method and an apparatus satisfying the low temperature fixing property and the high releasability are obtained by using toner in which a releasing agent having a melting point of from 60 to 120 °C is caused to be contained in an amount of from 1 to 20 wt%.

[0186]

(8) According to the inventions of claims 9 and 24, an image forming method and an apparatus satisfying the low temperature fixing property and the high releasability are obtained by using toner in which particles having dispersion diameter sizes of a releasing agent in toner are from 0.1 to 3  $\mu\text{m}$  occupy 80 % by number or more, and presence of the releasing agent is dispersed in the vicinity of particle surfaces by TEM observation.

[0187]

(9) According to the inventions of claims 10 and 25, an image forming method and an apparatus satisfying the high releasability are obtained by using toner showing viscoelastic property in which a storage modulus  $G'$  of toner is in a range of from  $5.5 \times 10^5$  to  $5.5 \times 10^7$  Pa at 80 °C and a storage modulus  $G'$  is in a range of from  $5.0 \times 10^2$  to  $1.0 \times 10^3$  Pa at 180 °C, and a maximum value of a ratio ( $\tan \delta = G''/G'$ ) of a loss modulus  $G''$  to the storage modulus is from 1.5 to 8.0 in a range of from 80 °C to 130 °C.

[0188]

(10) According to the inventions of claims 11 and 26, an image forming method and an apparatus satisfying the low temperature fixing property are obtained by using toner containing a binder, resin having an acid value of from 1 to 50 mg KOH.

[0189]

(11) According to the inventions of claims 12 and 27, an image forming method and an apparatus satisfying the low temperature

fixing property and the high releasability are obtained by using toner containing a binder resin having a glass transition point of from 40 to 60 °C.

[0190]

(12) According to the inventions of claims 13 and 28, an image forming method and an apparatus satisfying the low temperature fixing property and the high releasability are obtained by using toner containing a binder resin having a THF-insoluble content of from 1 to 20 %.

[0191]

(13) According to the inventions of claims 14 and 29, an image forming method and an apparatus satisfying the low temperature fixing property and the high releasability are obtained by using toner in which a main peak exists in a region of the molecular weight of from 2,500 to 10,000, and the number average molecular weight is in a range of from 2,500 to 50,000, in molecular weight distribution of a tetrahydrofuran-soluble content of a polyester resin contained in toner.

[0192]

(14) According to the inventions of claims 15 and 30, an image forming method and an apparatus satisfying the low temperature fixing property and the high releasability are obtained when the toner is obtained by dissolving or dispersing, in an organic solvent, a prepolymer formed of a polyester resin having an isocyanate group, a compound capable of elongating or crosslinking with the prepolymer, and a toner component to cause the dissolved or dispersed matter to perform a crosslinking reaction and/or an elongation reaction in an aqueous medium, and removing the solvent from an obtained dispersion liquid.

[Brief Description of the Drawings]

[Fig. 1] Fig. 1 is a pattern diagram showing an example of belt fixing.

[Fig. 2] Fig. 2 shows a diagram for explaining



spindle-shaped toner.

[Reference Numerals]

(Fig. 1)

An example of a pattern diagram of belt fixing

1 Heating roller	2 Fixing roller
3 Fixing belt	4 Pressure roller
5 Heat source	6 Oil application roller
7 Temperature sensor	8 Guide
P Transfer paper	T Toner

[Name of Document] Abstract of the Disclosure

[Abstract]

[Objectives of the Invention]

To provide an image forming method and an apparatus for forming an image by particularly using a belt fixing method, and toner for electrostatic image development.

[Means for Achieving the Objectives]

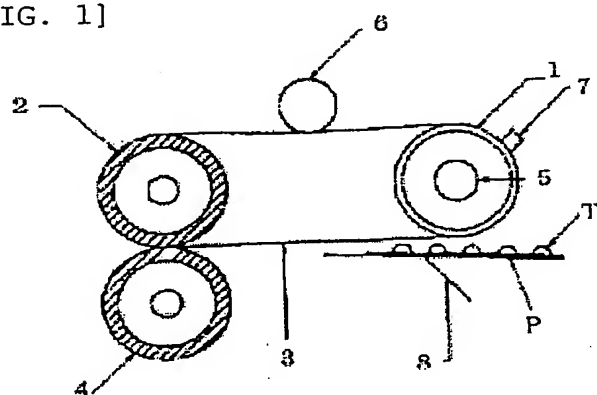
An image forming method and an apparatus using a fixing method for heating and fixing a toner image on a recording medium by a heating element, and one or more heating media heated by the heating element and a pressure member for causing the recording medium to be in press contact with one of the heating media, the image forming method and the apparatus being characterized in that at least one of the heating media is a belt-shaped heating medium used by being applied with a fixed amount of oil or no oil on a belt, and toner containing at least a binder resin and a releasing agent as main components is used, wherein the toner has a weight average particle size of from 3.0 to 7.0  $\mu\text{m}$ , particle size distribution of  $1.00 \leq D_v/D_n \leq 1.25$  ( $D_v$ : weight average particle size,  $D_n$ : number average particle size) and an average value of a shape factor SF-1 of from 100 to 150, and contains toner particles having SF-1 of 160 or more in an amount of 10 % by number or less.

[Selected Drawing] Fig. 1



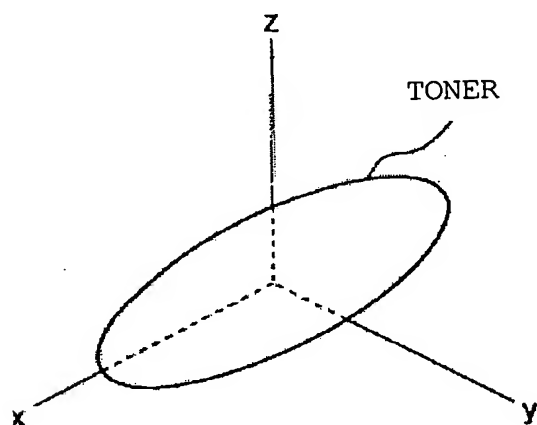
[Name of Document] Drawings

[FIG. 1]



[FIG. 2]

(a)



(b)

